

DECONTAMINATION FOAM FOR CHEMICAL SPILL MITIGATION

A Dissertation

by

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ABSTRACT

The release of hazardous chemicals poses a threat to individuals in the area of a release and to responders who attempt to limit the damage of the release. For a liquid phase spill, the most common decontamination technology is a sodium hypochlorite and water solution. Although this solution has been proven effective against a variety of contaminants, it also has a host of drawbacks. Therefore, there is a need for an industrial decontamination solution that is noncorrosive, nontoxic, nonflammable, and environmentally safe. The military has developed a solution using hydrogen peroxide as well as a quaternary ammonium complex that is currently used to decontaminate chemical and biological warfare agents, which may be adapted to fit the needs in industry. Additionally, turning this liquid solution into foam may prove even more effective while reducing the cost.

In order to test foam application, a foam generator was built in house. This foam generator was newly designed and built with features allowing for the study of foam production. A protected derivative of cysteine was chosen as the surrogate for a hazardous industrial contaminant. This derivative allowed for the study of non-polar decontamination due to the attachment of non-polar functional groups to the cysteine molecule. Liquid phase decontamination was conducted using both decontamination foam solution and decontamination solution without surfactant. All reaction analysis was carried out using GC-MS to determine the extent of reaction. The decontamination effect

was conducted using the foam generator and a test apparatus, which were able to show the successful decontamination of the contaminant in as little as 20 minutes.

DEDICATION

To my parents, Lisa and David Harding, to my sister, Barbara Harding, and to my wife Amy Harding.

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NOMENCLATURE

PSI	Pounds per square inch
Decon	Decontamination
H ₂ O ₂	Hydrogen peroxide
GC	Gas chromatograph
MS	Mass spectrometer
HCl	Hydrochloric acid
H/LDPE	High/Low density polyethylene
TCME	N-(tert-Butoxycarbonyl)-L-cysteine methyl ester
HE	High-expansion foam concentrate
FS	Foam solution
DS	Decontamination solution
DFS	Decontamination foam solution
QAC	Quaternary ammonium complex
DS2	Decontamination solution 2
EPA	Environmental Protection Agency

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1. INTRODUCTION

1.1 Releases

Accidental releases of hazardous chemicals in industry are a long-lasting major problem threatening people's health and the environment. Although lessons from well-known industrial tragedies such as the Bhopal Disaster in 1984 which killed thousands of people have been learned, undesired releases of chemicals continue to occur ¹. According to a report by the Bureau of Labor Statistics, in 2014 there were approximately 13,840 total cases of lost-time incidents caused by chemicals and chemical products in the U.S. ². A report from the U.S. Environmental Protection Agency (EPA) shows a significant increase in Total Recordable Incidents of chemical releases. In Region 10 (Idaho, Oregon, Washington, and Alaska), toxic chemical releases have increased by 940 million pounds between 2009 and 2010 ³.

The remediation of chemical releases is highly dependent on the specific hazards (*e.g.*, flammable, toxic, reactive) of the released chemicals. Foam application is one common approach used to mitigate the risks of certain released hazardous chemicals, mainly flammable liquids, but recent research has shown the great potential of foams in treating toxic chemical spills as well ⁴.

Decontamination is the treatment and neutralization of the hazards of chemicals, biological compounds, radioactive compounds, or other hazardous materials. In chemical decontamination, the mechanism of decontamination varies, but the most popular approach is the oxidation of the hazardous compound by nucleophilic attack ⁵. The goal of any decontaminant is to quickly and thoroughly mitigate the damage of a

hazardous chemical release. In order to cause as little secondary damage as possible, it is important for decontaminants to be noncorrosive, non-toxic, nonflammable, and environmentally friendly ⁶. Additionally, during the oxidation reaction, all byproducts must be sufficiently innocuous to allow safe clean up by personnel ⁶.

Decontamination (decon) foam solutions are composed of three main components: solvent, surfactant, and active decontaminant. Typically, the solvent is water and the active decontaminant is any combination of organic peroxides and quaternary ammonium complexes (QACs) ⁷. When combined with air, this solution forms a stable decon foam. Decon foams were originally developed to decontaminate chemical and biological warfare agents such as VX, sarin, soman, and sulfur mustard, by oxidizing such agents to non-hazardous products. Although a similar mechanism could also be applied to treat hazardous chemicals in industries, this technology has been slow to transition into the industrial sector. The majority of previous work focused on the development of decontamination solutions and foams for chemical and biological warfare agents ⁷⁻¹⁵, while the investigations on developing decontaminants for industrial spills are very rare ^{16,17}. Moreover, among these few studies, the efforts mainly focused on neutralizing polar hazardous chemicals, and the tests on non-polar contaminants did not explain the underlying dissolution issues.

1.2 Decontamination

1.2.1 History

Decontamination of hazardous materials is not a new concept. The first use of decontamination technology against a chemical or biological warfare agent was in 1915

at the battle of Ypres in World War I ¹⁵. Early decontamination technologies consisted of bleaching powders or other sources of sodium hypochlorite. Although sodium hypochlorite can be effective as a rudimentary decontamination technology, it has two main shortcomings. The first is that sodium hypochlorite is a hazardous chemical with a health rating of 3 and a reactivity of 2 on the NFPA fire triangle ¹⁸. This rating means it can cause damage to people, equipment, and the environment. The second is that exposed sodium hypochlorite loses its effectiveness over relatively short times. For military uses when the threat is apparent, this is not much of an issue, but in industrial application where the decontaminant may be stored for long periods of time until required, long term stability is necessary.

As time went on, other technologies began to develop to address some of the shortcomings of bleach. The first variation was a buffered bleach solution that focused on maintaining the chemical activity of bleach, even when stored for long periods of time ¹⁵. Although bleach is highly effective in general, it is harmful to equipment, wiring, and personnel, and it is ineffective at decontaminating in cold environments. For these reasons primarily, the military worked to develop a decontamination option that was less corrosive but that still maintained its effectiveness. The first non-bleach based technology was called Decontamination Solution 2 (DS2) and was adopted in 1960 ^{12,19}. The next major innovation was the invention of a foam decontamination solution. The major advantage of foam as a decontaminant is the high expansion ratio, *i.e.*, the ratio of the total volume of the foam to the volume of the liquid used to make the foam. This characteristic allows the decontamination foam to either cover large areas without using

as much solution or fill large spaces to decontaminate walls, ceilings, or even air space that liquids cannot reach. One of the earliest foams was developed by Cronce in 2000⁸. Since then, other decontamination technologies have been developed, but variants of bleach persisted throughout the years due to their ease of application and effectiveness at decontaminating a wide variety of chemical and biological warfare agents as well as many common household and industrial chemicals. Currently, sodium hypochlorite solutions are the most widely used decontaminants in industry, lab setups, and in the home²⁰.

Many of the more recent advances in the area of decontamination came from Cronce *et al.*^{6-8,21}. In 1996, Cronce developed a decontamination solution that was non-toxic, non-flammable, non-corrosive, and environmentally safe using quaternary ammonium complexes (QACs) as the main decontaminant⁶. QACs have long been recognized as effective disinfectants and are commonly used in the food service industry¹¹. The next generation of decontamination solution was developed in 1997 and combined the properties of QACs and hydrogen peroxide, both of which had previously proven effective as decontaminants⁷. Further advancements by Cronce involved turning the decontamination solution into decontamination foam by adding Knockdown® or other foam components used by firefighters in firefighting foams⁸. Building on the work of Cronce and the decontaminating properties of that foam, further effort was put into extending the lifetime of decontamination foams. One of the earlier forays into this area was a patent filed in 2003 by Faure *et al.*⁹. In this work, a foam that was created to decontaminate chemical, biological, and radiological hazards was taken as the reference

and treated to increase stability. Although many methods were shown, the most effective method was the addition of xanthan gum. Even in small amounts (1g/L), xanthan gum was able to provide anywhere from a three to five fold increase in the life and half-life of foams. Another related work was in a patent filed by Demmer *et al.* in 2006, where a foam that could decontaminate chemical and biological hazards was treated with a strong focus on increasing the stability of decontamination foam ²². In this work, surface tension was improved through the addition of gelatin at around 3% m/m. Also, the pH of the stabilized foams was much lower than decontamination foams typically used, generally in the range of pH 0.3–4.5 due to the addition of affinity-shifting chemicals such as acetic acid. Increasing the surface tension of the foam not only contributed to increased stability, it also contributed to decreased vertical slip on surfaces, which is very useful when spraying foam on walls, ceilings, and other surfaces where gravity might overcome the adhesive force of the foam. At present, the two main focuses of decontamination research are increased chemical activity of the decontamination foams or solutions, and increased surface tension and stability of the foams.

1.2.2 Chemistry

The chemistry of the decontamination reaction is highly dependent on the specific contaminant and decontamination technology. The first iteration of this work focused on the use of hydrogen peroxide as the oxidizing agent and cysteine, shown in Figure 1, as the contaminant, therefore the emphasis was on the reaction between hydrogen peroxide and high volatility thiols (namely cysteine). The reaction network for the oxidation of cysteine has been thoroughly studied in biology due to the reaction's

importance in the human body. In a paper by Luo *et al.*²³, this reaction was studied closely to determine the reaction products, reaction stoichiometry, and the reaction mechanisms. The main reaction is a cysteine to cystine reaction and is shown in Figure 2.

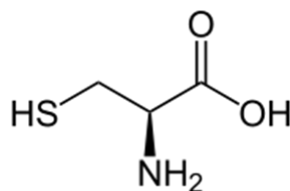


Figure 1. Cysteine molecular structure

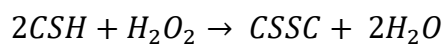


Figure 2. Cysteine hydrogen peroxide reaction²³

This reaction is composed of the reactions in the scheme shown in Figure 3.

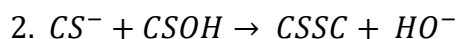
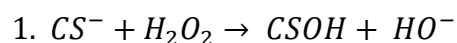


Figure 3. Reaction scheme for cysteine oxidation²³

In this reaction scheme, the proposed mechanism is a two-step nucleophilic attack. The sulfur atom in cysteine has two lone pairs of electrons that can be used for

nucleophilic attack. In the first step, the sulfur in the thiolate ion bonds to the hydrogen peroxide forming cysteine sulfenic acid. In the second step, another thiolate ion bonds to the cysteine sulfenic acid forming cystine. In this reaction scheme, the first reaction is the rate limiting step due to the relatively slow formation of cysteine sulfenic acid which is a reactant in the second step. It is important to recognize that this reaction is in the aqueous phase and takes place in the absence of any metal ions, which can catalyze thiol autoxidation. The reaction kinetics for this reaction are included below in Figure 4. Concentration of cysteine and hydrogen peroxide were independently adjusted in order to determine their influence on the rate. The results of this experiment were first-order with respect to each reactant. Additionally, pH was varied, and the results show that the reaction takes place fastest at pH 10.

$$\begin{aligned} \frac{-d[CS^-]}{dt} &= k_1[CS^-][H_2O_2] + k_2 [CS^-][CSOH] \\ \frac{-d[HOOH]}{dt} &= k_1[CS^-][H_2O_2] \\ \frac{d[CSOH]}{dt} &= k_1[CS^-][H_2O_2] - k_2 [CS^-][CSOH] \\ \frac{d[CSSC]}{dt} &= k_2 [CS^-][CSOH] \end{aligned}$$

Figure 4. Reaction kinetics for cysteine/hydrogen peroxide reaction ²³

Although there is no consensus on the reaction stoichiometry and kinetics, this proposed reaction mechanism is the most commonly accepted. Another proposed mechanism is

that the reaction is mainly free-radical dominated ²⁴; however, most groups have generated data consistent with the two-step nucleophilic substitution.

When hydrogen peroxide is in large excess, the following reaction scheme (Figure 5) takes the place of the first scheme (Figure 3). In this scheme, the hydrogen peroxide competes with cysteine species to form cysteine sulfinic acid and cysteine sulfonic acid. Additionally, Luo *et al.* noted that the scheme in Figure 5 does not entirely account for the final concentrations seen in their work. Their hypothesis is that there are other reactions taking place that form cystine, namely the hydrolysis of thiolsulfinate to produce cysteine, which is then available for additional reaction as shown in the scheme in Figure 3. This thiolsulfinate hydrolysis is supported by Sohn and Rudolph ²⁵

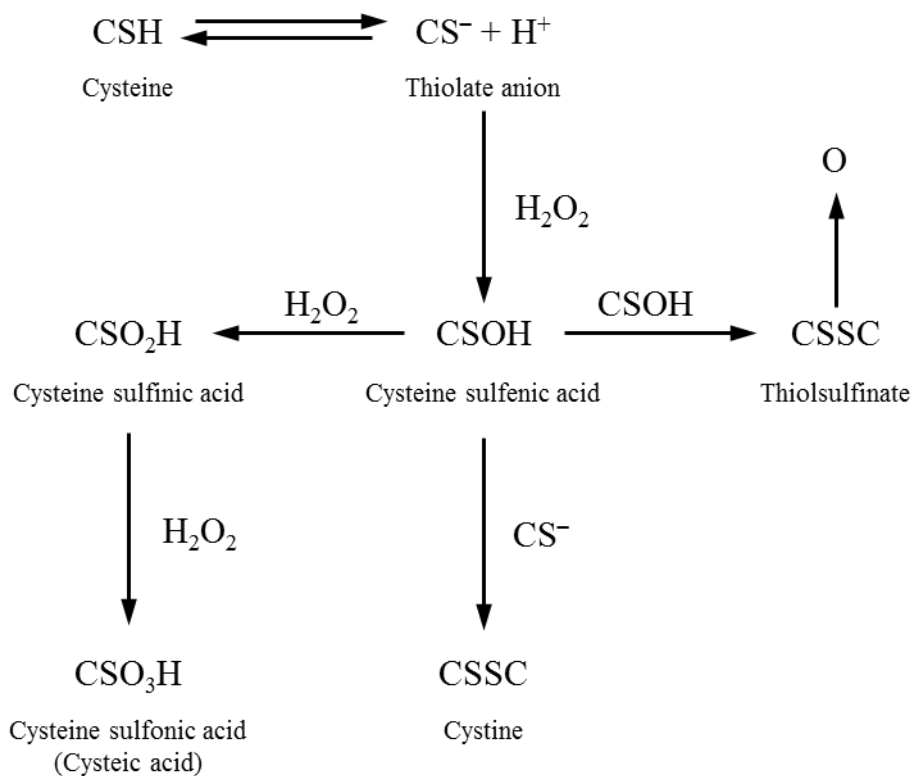


Figure 5. Full oxidation reaction network for cysteine/hydrogen peroxide reaction in excess hydrogen peroxide²³

It is also important to note that cystine has a very low solubility in water, which causes it to precipitate out of solution and decreases the formation of cysteic acid. Decreasing the pH of the solution by adding a small amount of acid increases the solubility of cystine significantly. By keeping the cystine in solution, it can further react with hydrogen peroxide and ultimately form cysteic acid.

GC-MS was used to measure the extent of the decontamination reaction. Cysteine is not ideal for GC-MS analysis due to its high melting and boiling point, which is a result of the terminal polar functional groups of the molecule. In order to

reduce the boiling point of cysteine for GC-MS analysis, a functionalized version of cysteine was used called N-(tert-Butoxycarbonyl)-L-cysteine methyl ester, abbreviated TCME, which is shown in Figure 6. This protected version of cysteine has a boiling point of 214°C, making it eligible for GC-MS.

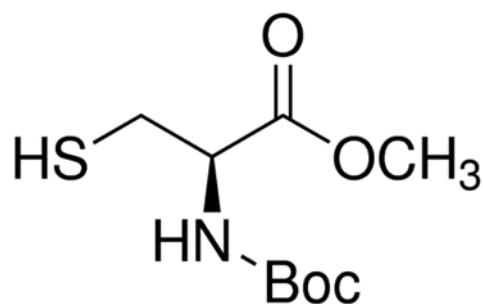


Figure 6. TCME molecular structure

TCME has the same basic structure as cysteine; however, instead of the carboxylic acid and amine group, it has a methyl ester and a tert-Butoxycarbonyl group, respectively. These two groups are both much less polar than the original terminal groups of the cysteine molecule, decreasing the melting and boiling point. This can be directly observed in the phase of these substances at standard temperature and pressure (STP); cysteine is present as a white powder at STP, whereas TCME is a colorless liquid.

Although TCME is much more ideal for GC-MS analysis, there are some drawbacks to its use. The first is that TCME is not prevalent in literature. As mentioned previously, the cysteine oxidation reaction has been studied extensively due to the importance of cysteine oxidation in the human body. In the case of TCME, oxidation

reaction pathways have not been published, meaning that some assumptions must be made. The first is that the reaction pathway for TCME is similar to that of cysteine. In cysteine oxidation, only the thiol is oxidized, resulting in a variety of intermediates and the final oxidation product, cysteic acid. In the case of TCME, the same thiol oxidation is expected, and the methyl ester and tert-Butoxycarbonyl should remain in their original form.

The second assumption is the formation of the disulfide bridge between TCME molecules during oxidation. This reaction occurs in cysteine and causes the dimer cystine to precipitate out of solution. In TCME oxidation, a precipitate is also observed, which forms only when H_2O_2 is present. Although this does not confirm that a TCME dimer is forming, it does lend support to that theory. Another measure of support is provided by GC-MS results. Pure TCME produces a reliable peak on the chromatograph; however, any oxidation products which form during the reaction do not, further confirming that TCME is reacting to form something that is either absent in solution or has a boiling point that is high enough or low enough that it will not elute through the column. The most likely scenario is that the TCME is indeed reacting to form an insoluble dimer, likely by the same means as cystine formation.

Another issue is the less polar nature of TCME, which affects its solubility in foam solution or water. Although the low polarity aids in GC-MS analysis, its ability to dissolve in the foam solution and subsequently react with H_2O_2 is crucial to decontamination. This point will be discussed in more detail in the results and discussion

section and is able to provide better insight into decontamination of less polar compounds, which is a gap in the literature.

1.3 Foams

1.3.1 General Info

Foams have many properties that can make them effective tools for first responders. They have a high resistance to heat flow, they block mass transfer, and they can quickly fill large areas²⁶. The high resistance to heat flow is due to the large amount of air trapped in the foam matrix. Because the foam bubbles are fairly small (dependent on the foam's expansion ratio and other conditions of the foam), the air inside the foam bubble cannot move freely, and therefore, heat must be conducted through the air, with an approximate thermal conductivity of $0.0271 \text{ W/m}\cdot\text{K}$ ²⁷. Foams can form layers greater than 1 meter thick, and that height is comprised almost entirely of air with a high resistance to heat flow. This property is highly effective in many different applications, especially firefighting.

Additionally, foams are very good at blocking mass transfer. This is due to the thick layers they form with many intermediate liquid surfaces, which prevent the convection of materials in the gas phase²⁶. This property is effective in blanketing volatile substances and substances that can easily be dispersed in the air. An example application is on fuming acids such as oleum, chlorosulfonic acid, chlorine dioxide, sulfur trioxide, and a variety of others²⁸. When the concentrations of some acids are high enough, the acid will fume. These acids often have violent exothermic reactions with water. In order to dilute the acid to below fuming concentration, water must be

added slowly. Foam is ideal for this treatment, because it covers the acid, preventing the fumes from spreading, and slowly dilutes the acid as the foam collapses.

Finally, foams can fill large spaces very quickly. This is due to the high expansion ratio of foams and their subsequent large volume. This function of foams can be used to cover large areas. Drumgoole showed the effectiveness of using the high air content of foam to fill an enclosure, which would then dampen the detonation of a dirty bomb or other terrorist device ²⁹. By filling the enclosure with foam, the high expansion ratio, in tandem with the many liquid/gas layers, absorbs the shock of the explosion, preventing the contents of the dirty bomb from dispersing.

1.3.2 Expansion Foams

The main use of expansion foams by firefighters is to combat liquid fires. Depending on the scenario, there are a variety of different foams to choose from. Below is a table depicting the different characteristics of foam (Table 1).

Table 1. Defining characteristics of foam

Expansion Ratio ³⁰	Foaming Agent ³¹	Proportioning Rate ³⁰
Low (<20:1)	Protein	1%
Medium (20:1 to 200:1)	Fluoroprotein	3%
High (>200:1)	Film forming fluoroprotein	6%
	Aqueous film forming foam (AFFF)	
	Alcohol-resistant AFFF	

Table 1 shows the three classifications of foams for use by firefighters. The first is expansion ratio, which is defined as the ratio of the total volume of the foam to the volume of liquid foam solution used to make the foam. In firefighting, foams with an expansion ratio less than 20:1 are called low-expansion foams, between 20:1 and 200:1 are called medium-expansion foams, and greater than 200:1 are called high-expansion foams³⁰. Each type of foam has advantages and disadvantages that make it more suited to different situations. Low-expansion foams can behave like low-viscosity liquids, which make them ideal for covering large surface areas quickly³⁰. Also, due to the lower air content and associated higher specific gravity, they are effected less by the wind and other adverse weather conditions³⁰. Additionally, they can be blasted or thrown similarly to water coming out of a fire hose³¹. Because their density is much lower than that of water, low-expansion foams have much less inertia and therefore cannot be blasted as far, but they can still be used on fires that are far away. On the other end of the spectrum, high-expansion foams are more useful when trying to fill a large volume because of the high expansion ratio³¹. If, for instance, there is a fire in a storage facility or a hangar, the foam can be used to quickly fill the structure without using large quantities of foam solution³¹. High-expansion foams cannot be blasted because of their very low density. These foams must be produced onsite in the area of application. Medium expansion foams have some of the applicability of each of the previous types. They can be blasted about 12 to 35 meters, depending on the expansion ratio, making them very versatile³².

There are three major ingredients in a foam: a gas, a liquid, and a surfactant. Without all three of these ingredients, foam cannot be made. In most circumstances, the gas is air and the liquid is water, so the chemistry of most foams differs due to surfactant selection, as well as any additives that may be in the foam³¹. Aside from the chemistry, foams can also differ by the proportion of the ingredients, which is expressed in proportioning rate and expansion ratio³¹. The two main types of surfactants used are hydrocarbon surfactants and fluorosurfactants³³. Hydrocarbon surfactants are used to maintain the integrity of the air-water interface. This function helps increase the foam volume and stability³¹. Fluorosurfactants can lower the surface tension of water much more effectively than hydrocarbon surfactants, so they are used specifically for this purpose³¹. On the other hand, fluorosurfactants do not have the same high foaming characteristics that hydrocarbon surfactants have, so these surfactants work much better in combination than separately³¹.

When applying a foam to a fire, the foam should be used at its prescribed proportioning rate. Proportioning rate is defined as “x parts of foam to be mixed with 100-x parts of water”³¹. Some common proportioning rates in firefighting are 1, 3, and 6 percent³⁴. Foam concentrates with lower proportioning rates have a higher concentration of active ingredients, meaning they can be further diluted with water and still maintain their effectiveness³¹. Proportioning the foam solution and water manually can be inaccurate and can take time and effort that often cannot be spared during a fire. In order to expedite the process, foam proportioning systems have been developed. Some of these are line eductors and self-educting nozzles³⁵. Eductors use the flow of water passing an

orifice to create a vacuum, thus pulling concentrate into the water³⁵. This method operates by the Venturi Principle. In this setup, a metering valve is used to control the foam concentrate flow. This valve can be adjusted for use with 1%, 3%, and 6% foam concentrates³⁵. In addition to proportioning, the foam nozzle can be either aspirating or non-aspirating³⁵.

Another application of expansion foam in the process industry is the hazards mitigation of LNG spills. Foam application for LNG spills can be used as either a preventative or protective measure. As a preventative measure, on one hand, the recent work reveals that the foam works by reducing the heat convection and radiation through the blanketing effect, thereby reducing the vaporization rate of the LNG pool^{36,37}. On the other hand, as LNG vapors pass through the foam zone, they are heated by contact with the much warmer foam, reducing the density of LNG vapor and thus minimizing the size of the ignitable LNG vapor cloud³⁸.

When the LNG pool has already been ignited, the foam can be used for mitigation as well, which works to suppress a fire by four major mechanisms. The foam smothers the fire, physically separates the flames from the fuel source, cools the applied objects, and reduces the ability for flammable vapors to come in contact with oxygen from the air³⁴. In high-expansion foam applications on cryogenic liquid fuels, the foam performs three of these tasks, but does not work to cool the fuel surface, as the temperature of the foam is much higher than that of the fuel; however, it does work to reduce the heat input through convection and back radiation of the flames³⁷. Although high-expansion foam generally cannot extinguish an LNG fire on its own, it suppresses

the fire, and it allows the fire fighter to approach the fire and apply other firefighting methods, *e.g.*, dry chemical. When the fire is ultimately extinguished by other means, any foam that is still present can take on a preventative role, serving to prevent reignition

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1.3.3 Decontamination Foams

Decontamination foams are comprised of a liquid, a gas, a surfactant, and a reactive component. Typically, the liquid is water, and the gas is air; however, in certain circumstances these can be substituted. The surfactant can be chosen from a variety of different options provided it will not react with the reactive component. The reactive component can be formed from one or more reactive chemicals. One of the more well-known reactive components is the combination of an oxidizer and a quaternary ammonium complex (QAC)⁸. The foam can also include other components such as pH adjustors, or buffers, and corrosion inhibitors. The foam developed by Cronce is nontoxic, nonflammable, and noncorrosive. The surfactant and reactive chemicals can be chosen from a wide variety of different options and should be selected by experts who are skilled in the art of decontamination. The surfactant used is typically an existing foaming component from firefighting. The selection of foaming component is not as specific as oxidizer or QAC selection, but it is usually an aqueous film forming foam (AFFF), such as Knockdown®⁸. Most oxidizers are peroxy or hydroperoxy compounds, and most frequently are hydrogen peroxide. A QAC is comprised of a nitrogen atom bonded to four alkyl or aryl groups through a carbon atom. They have the form $N(R)(R')(R'')(R''')$ ⁸. The most effective QACs are chloride salts of

benzyltriethylammonium and benzyltrimethylammonium ^{6,7}. Along with the oxidizer, the QAC is used to decontaminate hazardous substances. One composition suggested by Cronce is presented in Table 2.

Table 2. Example decontamination foam composition ⁸

Component	Weight Percent	Function
Benzyltrimethylammonium Chloride	13%	QAC
Isobutanolamine	20%	Corrosion Inhibitor
Toluenesulfonic acid	27%	pH Adjustor
Hydrogen Peroxide	20%	Oxidizer
Knockdown®	20%	Foaming Component

The weight percentage of each component is highly variable based on the desired outcome of the foam. If rapid decontamination is required, the QAC and oxidizer amount can be increased. If foam stability is desired, the foaming component can be increased. If a certain pH is more effective against a particular contaminant, then the pH adjustor quantity can be changed. Cronce provides the maximum ranges, suggested ranges, and ideal ranges of each component for his particular foam ⁸. Aside from the weight percentage of each individual component, the QAC/foaming component ratio is also important. Generally, any ratio between 2:1 and 1:2 forms a suspension instead of forming an ideal foam ⁸. Suspensions cause the foam to be ineffective because the dispersion of the QAC in the foam is not uniform, resulting in a foam with poorer stability and less decontaminating efficiency than the ideal.

There are five crucial characteristics of a decontamination foam. These are decontaminating effectiveness, foam stability, expansion ratio, the formation of non-hazardous products, and what can be grouped as secondary effects (toxicity, flammability, corrosivity, and environmental safety). Decontaminating effectiveness is important because the foam must be able to neutralize the contaminants by reacting with them to produce less harmful compounds. The faster this reaction happens, the faster the spill can be cleaned. Also, if the decontamination process is more effective, less foam will be required for a given spill. The reactivity of the active component of the foam is very important. Increasing foam reactivity increases the rate at which the contaminant is converted to the less harmful product, reducing the likelihood of an injury or fatality. However, allowing a foam to be too reactive can have adverse consequences. If foams are too reactive, they can damage electronics, equipment, surfaces, and people and may cause excessive damage. In order to achieve quick decontamination without causing unnecessary damage, foam reactivity must be in a safe yet effective region.

Foam stability is important because the foam must be able to maintain its structure long enough to decontaminate the spill. If the foam collapses before the decontamination is complete, then the foam/contaminant interface may not be present and the foam will fail to neutralize the contaminant.

Expansion ratio is important because it is the property that distinguishes a decontamination foam from other liquid decontaminants. Trapping the correct amount of air in the liquid matrix gives the decontamination foam all of the added properties of foams such as blanketing effect, three dimensional decontamination, and greatly reduced

reactant requirements. The correct expansion ratio must be determined for each application, but typically a ratio between 20:1 and 50:1 is recommended¹⁴. Expansion ratios below 20:1 can become too heavy and thus unstable as well as requiring too much foam solution to cover a spill. Expansion ratios over 50:1 can result in a lack of available reactants at the foam/contaminant interface, slowing the reaction. Additionally, expansion ratios that are too high are very difficult to spray onto spills because their density is too similar to that of air. When the correct expansion ratio is achieved, the foam will have enough reactants present to decontaminate spills, but will also be stable and able to be blasted 20 to 50 feet onto spills³².

The formation of non-hazardous products is especially important. The goal of decontamination foams is to treat hazardous chemicals and convert them into something that is much less harmful than the original contaminant. If the foam instead turns one harmful chemical into another, then although the decontamination reaction has taken place, in practice a contaminant is still present.

The last important characteristic is a group of properties termed secondary effects. Ideally a foam should be non-toxic, non-flammable, non-corrosive, and environmentally safe. If the foam cannot meet these criteria, then it will introduce new hazards to the system, which will complicate the cleanup procedure.

The end goal of decontamination foam application to a contaminated area is as follows. First, any contaminant contacted by the foam should be neutralized in a short amount of time. Second, the foam should be stable enough to maintain contact throughout the reaction. Third, the foam should have a high enough expansion ratio to

provide sufficient coverage of the contaminant without using excess foam solution.

Fourth, the chemical reaction should only produce compounds that are safe enough for emergency responders to enter the area without undue risk to themselves. And fifth, the foam should not introduce any new hazards to the area in which it is applied.

2. PROPOSED PROBLEMS

2.1 Development of a Lab-Scale Foam Generator

A suitable foam generator was required to perform decontamination foam testing. After looking at many commercially available foam generators³⁹⁻⁴², it was determined that they would not meet the needs of the experiment. The main issue with the commercially available foam generators was an excessively high foam generation rate. There were also secondary issues such as a lack of customizability, water discharge on startup, and their dependence on hydraulic power, which would have required additional utilities. Due to the maturity of foam generation, there were many previous patents that provided guidance on features that should be included in the foam generator⁴³⁻⁴⁸. One of the main sources of information was NFPA 11; Standard for Low- Medium- and High-Expansion Foam³⁰.

2.2 Decontamination Foam Application to an Analog of Industrial

Contaminants

Although decontamination is a relatively old field, it is a field in which there has been very little research conducted. A majority of the work has been either in patents, verification of decontaminants, or review papers. Additionally, although there have been many contributions to reactions happening in the liquid phase, there is very little concerning reactions happening in the foam phase. There are substantial gaps in the understanding of important factors in foam decontamination that formed the motivation for this work.

2.3 Proposed Problems

2.3.1 Research Gaps

As mentioned previously, foams have been used for many years; however, there are still gaps in foam research in both the LNG field and decontamination field. One of the major gaps in LNG research is the understanding of the physical interaction between the foam and the LNG system in lab-scale tests. In decontamination research, experimentation has been fairly minimal due both to the recent nature of the technology^{8,14,17} and the highly hazardous chemicals used as the contaminant in decontamination experiments⁴. In order to conduct these experiments, an improved lab-scale foam generator was developed to meet the research demand.

In a fire scenario, the application rate of the firefighting agent *i.e.*, water, dry chemical, or foam, is a crucial factor in extinguishing an existing fire or preventing a fire from spreading. For this reason, industrial foam generators are constructed to apply foam at a very high rate. One example generator, the Chemguard 1500WP foam generator, has a minimum flow rate of 38 m³/min³⁹. Compared to some other foam generators this value is relatively low⁴⁰⁻⁴². Additionally, in order to increase the applicability of the foam generator, hydraulic power is typically used. Because fire codes require fire water to be pumped throughout the facility and accessible from fire hydrants at regular distance intervals⁴⁹, pressurized water is widely accessible in an industrial facility, which makes using hydraulic power an excellent approach.

Although commercially available foam generators are suitable for foam application in industry, there are drawbacks of using them in a research setting. The

most obvious problem is the foam application rate. During foam application on an industrial spill, high foam application rate is beneficial to cover the spill quickly; however, the same application rate is far too high for lab-scale research. In an LNG spill scenario, characteristic foam depth for an LNG spill is anywhere from 0.45m to 0.91m⁴⁹. Assuming a floor area of 55m², which is typical for a research lab, even at the minimum setting the foam from these commercially available foam generators would fill the lab to a depth of 0.5 m in 43 seconds. Additionally, industrial-scale foam generators are powered by pressurized water, which causes two operational problems: the requirement for a large volume of pressurized water and excessive water discharge that accompanies the introduction of water during startup. The dependence on pressurized water also poses a safety issue created by having a pressurized system. The pressurized water requirement limits the availability of such equipment only to areas where pressurized water is accessible. In certain applications water discharge during startup is tolerable; however, when applying the foam to cryogenic liquids, the excessive water discharge causes rapid vaporization of the liquid, which compromises the objective of foam application. Moreover, commercial foam generators provide little working flexibility aside from changing hydraulic pressure³⁹⁻⁴². Some dependent variables such as foam application rate, foam expansion ratio, and foam bubble size are important in research on foam functionality. The fact that these variables are inextricably related with others requires independent control of each parameter to study the effect of an individual variable on foam functionality. Therefore, it is desirable to be able to manipulate those variables in an organized manner from the standpoint of experimental design. The

ultimate purpose of this work is to provide a feasible design for a research-scale foam generator and to discuss several key parameters of foam functionality such as foam expansion ratio, time to half height, and foam application rate associated with such a design. Utilizing the design proposed in this work will help disclose the effect of individual variables on foam performance for different applications in the future including LNG spill control, decontamination, and fire suppression.

Decontamination foam application has many gaps in understanding. Some of these gaps are application of decon foam to industrial contaminants, an understanding of the interaction between decontamination foam and non-polar contaminants, an understanding of the effect of surfactant on foam reactions occurring in the liquid phase, and application of foam to spills using a foam generator. Love *et al.*⁴ conducted one of the most comprehensive decontamination foam studies; however, his work was mainly focused on verifying the decontaminating effect of existing decontamination foams on chemical and biological warfare agents which were applied to a variety of different materials, and no fundamental conclusions were made about the foams. Besides Love's work, there is very little on decontamination foam in peer-reviewed journals, with the majority of the literature coming from review papers and patents. One patent does mention industrial contaminants and provides some data on their decontamination¹⁷. Although the provided information is valuable, patents are intentionally written ambiguously, making it difficult for the author's work to be recreated or verified.

Many contaminants on which decontamination foams may be used are non-polar; however, literature has mainly considered polar contaminants. The issue with non-polar

contaminants is that they have difficulty dissolving in water, which is the base of the foam solution. In order for the decontamination reaction to occur, the contaminant and H₂O₂ must come in contact, which requires the contaminant to be dissolved in the foam solution. Although tests have been conducted to determine the decontaminating ability of various technologies such as liquid decon solutions and decon foams, there is no literature on the effect that the surfactant has on decontamination in the liquid phase. Although this may have little effect when the contaminant is polar, for non-polar contaminants the presence of surfactant may be important in improving dissolution. Lastly, in the majority of papers in literature, such as the paper by Love *et al.*⁴, the foam is mixed and applied by hand, which has an influence on the foam structure and may provide results that do not reflect realistic application. By using a foam generator, many properties of the foam can be controlled and no damage will be done to the foam matrix due to excessive agitation.

This work attempts to address some of the gaps in decontamination foam, chiefly decontamination of non-polar chemicals that are analogs for industrial contaminants in both the liquid phase and the foam phase. In reaction kinetics, both transport and reaction are key factors, and the transport component of decontamination has not been studied. By using TCME and a self-made foam that is very similar to commercially available foams this transport issue can be studied.

2.3.2 *Research Objectives*

The motivation of this work was to develop a foam generator suitable for lab-scale foam generation and use that generator to apply existing foam decontamination

technologies to industrial chemical spills. Existing decontamination foams have extraordinary properties which can be applied to slightly different chemicals in the industrial sector. By using this existing technology in a novel application, chemical hazards may be mitigated, ultimately reducing the consequences of chemical spills and saving lives.

3. LAB-SCALE FOAM GENERATOR*

3.1 Introduction

In order to conduct foam trials in the lab, a new lab-scale foam generator was built. The model for the foam generator was based on the low-flow high-expansion foam generator provided in NFPA 11³⁰. The original design for the apparatus shows the basics of how to construct such a device, but leaves a lot of the design decisions up to the researcher. A picture of the device shown in NFPA 11 is presented below in Figure 7.

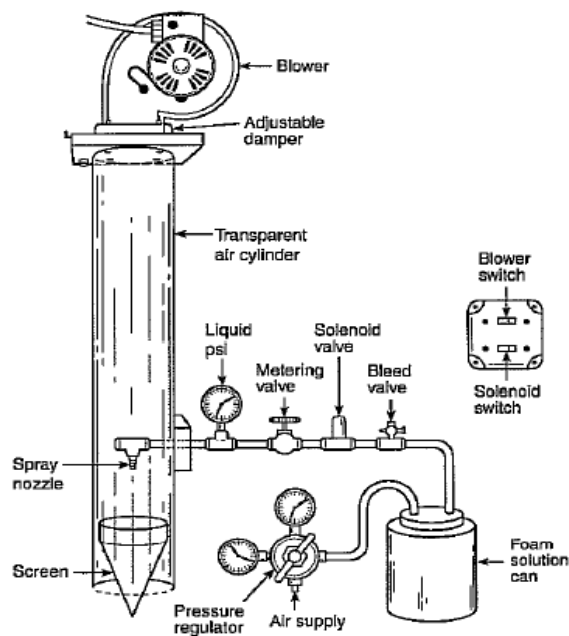


Figure 7. High-expansion foam quality test generator³⁰

*Reprinted with permission from “Improved research-scale foam generator design and performance characterization” by Harding, B., Zhang, B., Liu, Y., Chen, H. & Mannan, M. S, 2016. *Journal of Loss Prevention in the Process Industries*, 39, 173-180, Copyright [2016] by Elsevier.

In the NFPA design, the foam solution is pushed through the pipes by backpressure from the air supply. The air supply pressurizes the foam solution can, forcing foam solution through the piping and out the spray nozzle. The foam solution is sprayed onto the screen where air from the blower moves through the screen creating foam bubbles. The apparatus also contains a pressure regulator to control the pressure of the air inlet, a metering valve to control the flow rate of the foam solution, and an adjustable damper to control the flow rate of the air. Additionally, there is a solenoid valve for remote control, a bleed valve to depressurize the system during shutdown, and a liquid pressure gauge to take more accurate pressure readings just before the nozzle. Pressure readings at this point are important because foam solution flow rate through the nozzle is a function of pressure, and having an accurate value as close to the nozzle as possible allows the most accurate flow rate information. The transparency of the air cylinder is not a requirement, but is a luxury that allows the researcher to see the nozzle and screen during operation in case any adjustments are necessary.

3.2 Materials and Methodology

3.2.1 Test Apparatus

From this original diagram, many changes were made to create an apparatus that was more in line with research applications. Some of the major changes were; the orientation of the transparent air cylinder, the inclusion of a pump, and the differences in the piping setup. The schematic of the new setup is shown in Figure 8 below and pictures of the setup are shown in Figures 9, 10, and 11.

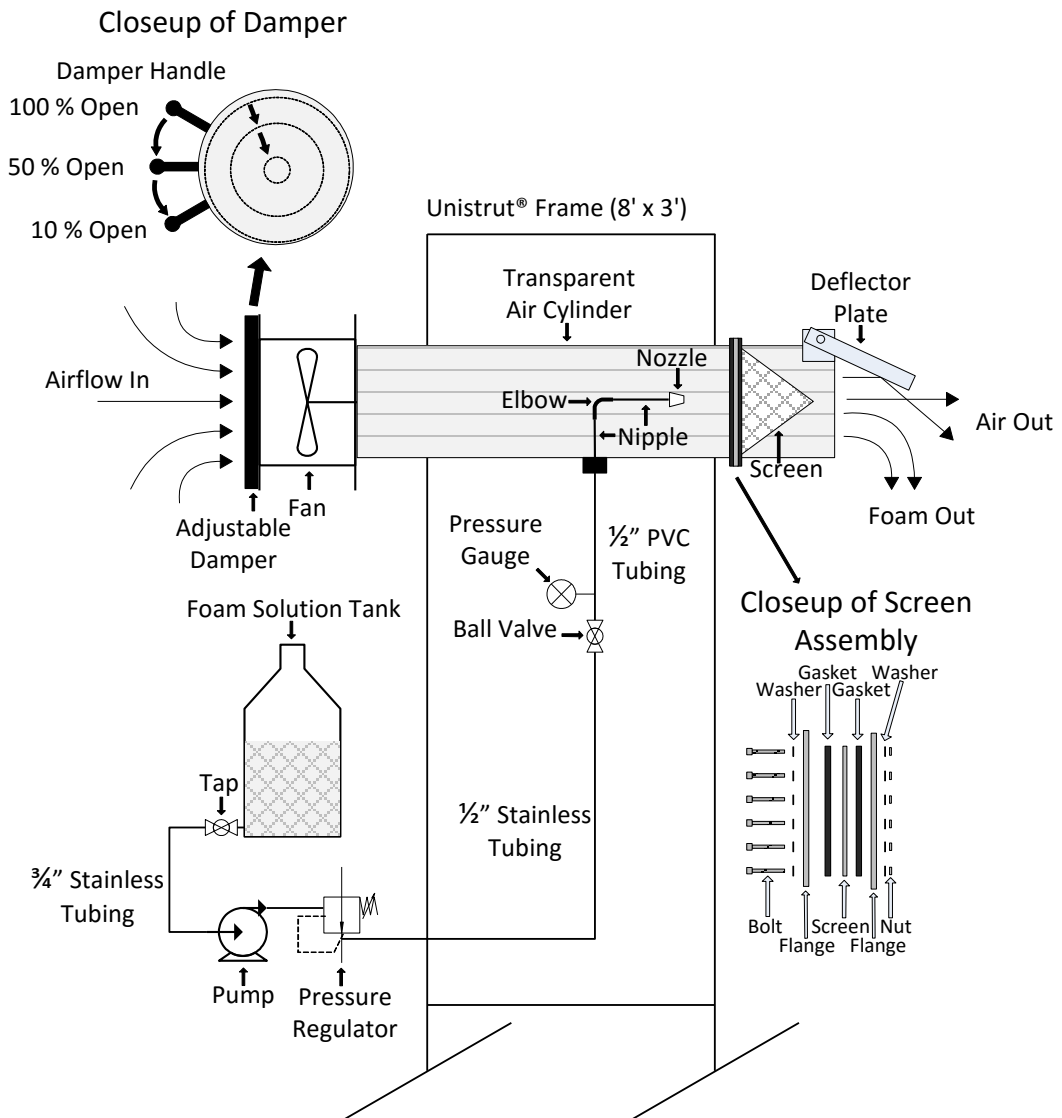


Figure 8. Diagram of foam generator used in experiments

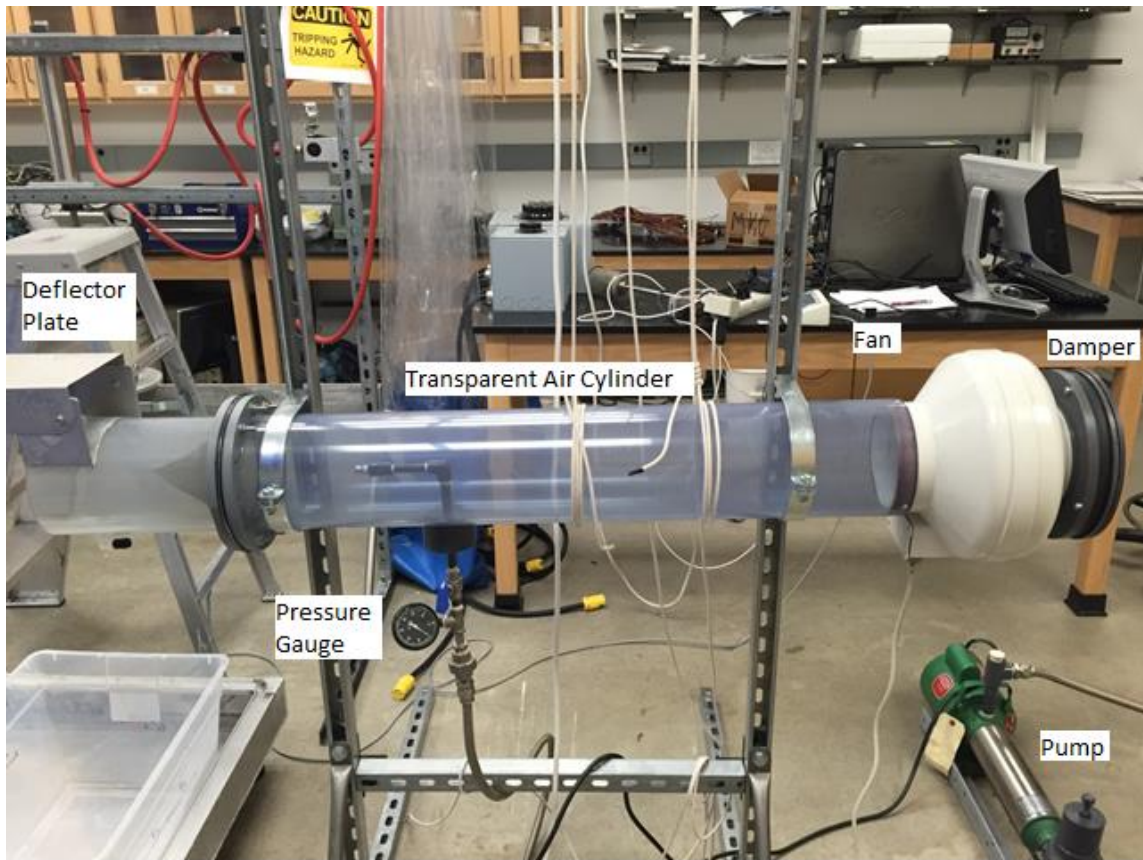


Figure 9. Picture of the foam generator with some important features labeled



Figure 10. Close-up picture of the iris damper in the 2.5% open position

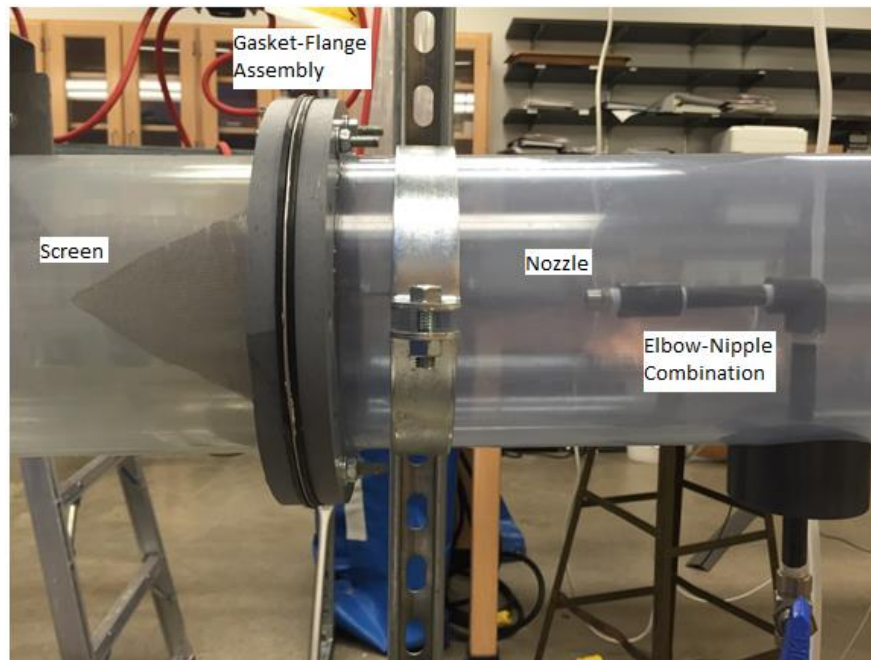


Figure 11. Close-up of the front end of the foam generator with some important features labeled

The horizontal orientation of the transparent air cylinder performs two functions. The first is that a horizontal setup allows foam to be carried by the air flow toward a target. This adjustment allows the flexibility of developing foam that is deposited into an expansion foam container, shown in Figure 12 directly beneath the foam solution or projected toward a location 10-15 feet away from the source. In order to direct the flow of foam, a deflector plate was installed at the end of the transparent air cylinder. The position of this plate can be changed to push the foam down at a variety of angles allowing the foam to be directed onto spills at various distances from the generator. Another benefit is the inclusion of the drain valve. In the vertical setup, any foam solution that is not converted into foam will fall into the container, as it is positioned directly below the screen. In the new setup, the excess foam solution settles in the

bottom of the cylinder underneath the screen. From there the foam solution flows through a hole and drips into a waste container. The drip tray is very useful in characterization of expansion ratio, as this metric is dependent on the mass of foam solution. Because the expansion ratio calculation is done by dividing the foam volume by the mass of foam solution used, any foam solution not converted to foam will increase the mass without increasing the foam volume, giving inaccurate data. In some applications, unconverted foam solution can also have detrimental effects²⁶. If unconverted foam solution is applied to an LNG pool, the large temperature difference between the foam solution and the pool and the high heat capacity of foam solution will cause additional LNG to evaporate, which is counterproductive to the application of foam.



Figure 12. Picture of the foam container and fence showing the scale located beneath it to measure the mass

The inclusion of a pump in the system is both a necessity and an improvement. During pressure testing, the foam solution tank, a 50 liter LDPE carboy from US Plastic Corp, was found to withstand around 28 psig before the cap deformed allowing air to escape. In order to achieve the desired foam solution flow rate, the system pressure must be able to reach at least 50 psig. To resolve this problem, the air supply was removed and a pump was added downstream of the foam solution tank to pressurize the foam solution. This new setup also has some advantages that the previous system did not. The first is that the system now only requires power to operate, meaning that it can be transported and used in areas that do not have a pressurized air source. By removing the pressurized air utility from the setup, it is much more conducive to conducting experiments in a different location. The second improvement is that the pump can boost the pressure much higher than the pressurized air. Because a majority of the setup is made from stainless steel and the PVC components can withstand 160 psi, running at higher pressures is a viable option. The third improvement is that the new setup is more inherently safe because the pump can be easily unpowered, quickly depressurizing the system, whereas with the pressurized air setup, the whole foam solution tank is under pressure, which must be vented.

The last major change is the difference in piping setup. In the original NFPA diagram, there is very little detail on how to actually assemble the apparatus. Many of the piping decisions were made during the planning and construction of the apparatus, some of which add to the functionality of the setup, and others which are simply required for the foam solution to flow through the system. One such addition is the 10

foot flexible PTFE/stainless steel hose. This addition allows the height of the air cylinder to be changed, permitting foam production into containers of different heights or the production of foam at different trajectories. Another addition is the elbow/nipple combination just before the nozzle. This section of the piping allows nozzle repositioning which ensures that the screen is properly coated with foam solution. Because the spray pattern of the nozzle may vary based on pump pressure, air velocity, and the flow properties of the foam solution, nozzle repositioning is important so that the screen can be fully coated with foam solution without spraying foam solution on the sides of the cylinder. There are also multiple nozzles and multiple screens with different mesh sizes that can be utilized depending on the application.

In order for the apparatus to be effective, it must be able to continuously produce high quality foam at the desired expansion ratio. In order to achieve this goal, many of the aspects of the apparatus must be adjustable to reach the desired foam production. Foam properties are dependent on a multitude of factors; however, certain properties are dominated by a few factors. The first is expansion ratio. This is dominated by the ratio of air flow to liquid flow with nozzle size (which contributes to uniform screen coverage) as a secondary characteristic. The second is foam production rate. This is dominated principally by air flow with liquid flow as a secondary characteristic. Other properties that are tougher to separate are foam stability and foam matrix bubble size.

3.2.2 Apparatus Operation

The apparatus was designed with ease of operation in mind, meaning there are very few steps required to create foam. First, the valve to the foam solution tank must be

opened, allowing the foam solution to flow to the pump, and the valve to the nozzle should be opened to prevent the pump from over pressurizing the piping. Next, the fan should be started and sufficient time should be given to allow the airflow to fully develop (5-10 seconds). Once airflow is developed, the pump should be started. Once those steps have been completed, the apparatus will produce foam. If the pressure must be adjusted, only the pump should run while a receptacle is held in front of the air cylinder to catch the liquid so that it does not fall in the container. When that is set up, the pressure can be adjusted to the desired level and the pump turned off. Once complete, the original procedure is followed. Likewise, if the damper is to be used, it should be set to the desired position and the original procedure followed.

3.2.3 *Experimental Approach*

In order to determine the quality of the foam that the new apparatus was able to produce, validation experiments were conducted. The first of these experiments examined the foam production limits of the apparatus. In this set of tests, the foam generating apparatus was operated at the boundaries of each control variable, *i.e.*, damper position and foam solution pressure. The limits of the foam solution pressure were determined to be 3-60 psi and the limits of the damper were 2% open to fully open. Below 3 psi the foam solution had insufficient pressure to flow through the nozzle properly and failed to create foam. For safety reasons, 60 psi was chosen as the ceiling. In terms of damper position, below 2% open there is insufficient air to create medium- and high-expansion foam. At any damper position between 2% open and 100% open foam can be produced.

After the operating boundaries were defined, they were narrowed to a range that would produce good quality high-expansion foam. The observable traits of interest are a high expansion ratio (>200) and a flow characteristic that moves with the pattern of the air stream and does not flow like a low viscosity liquid. With the damper fully open, the pressure was incrementally increased by 10 psi, thereby increasing the foam solution flow rate, until the foam no longer met these criteria. When the pressure reached 45 psi, the foam no longer moved along with the stream of air coming from the fan, it began to flow over the bottom lip of the air cylinder. This change in flow characteristics is due to the increased density of the foam and is a function of the higher foam solution to air ratio. The minimum pressure that produced foam was in the range of 3 psi. The exact value is difficult to determine because foam production changes from continuous to intermittent with extremely low flow rates. With these boundaries defined, the testing increments were selected. The final experimental plan was as follows.

Foam solution pressures: 5, 10, 20, 30, 40 psi

Damper positions (percentage open): 100%, 50%, 25%, 12.5%

The output variables for each trial were expansion ratio, time to half-height and foam production rate. Expansion ratio was calculated by determining the difference in the mass of the foam container before and after foam addition and dividing that value by the volume of the container and the density of water.

$$Expansion\ Ratio = \frac{Mass_{Tank,Initial} - Mass_{Tank,Final}}{Volume_{Tank} \times Density_{water}}$$

Equation 1. Foam expansion ratio calculation

If the foam did not fill the container evenly, the container volume was corrected to a reasonable value by estimating the average height of the foam. Time to half-height is defined as the time the foam takes to settle to half of its original height. The foam addition and subsequent collapse has been captured by video camera for each experiment and analyzed to determine the time to half-height.

3.2.4 Procedure

During each experiment, the scale was used to capture the mass of the container and its contents. Data analysis was conducted after the experiment to measure the mass addition and the time required to fill the container. With that information, the expansion ratio and foam volumetric flow were calculated. Each run was filmed using a video camera, which was able to determine the time to half-height. Additionally, one trial was analyzed using Matlab to determine the height as a function of time throughout the trial.

3.3 Results

Foam was produced and characterized using the foam generating apparatus and was analyzed on the basis of three important characteristics. These three characteristics were expansion ratio, time to half-height, and foam production rate. Additionally, pictures of the foam were taken for reference and are included in Figure 13.

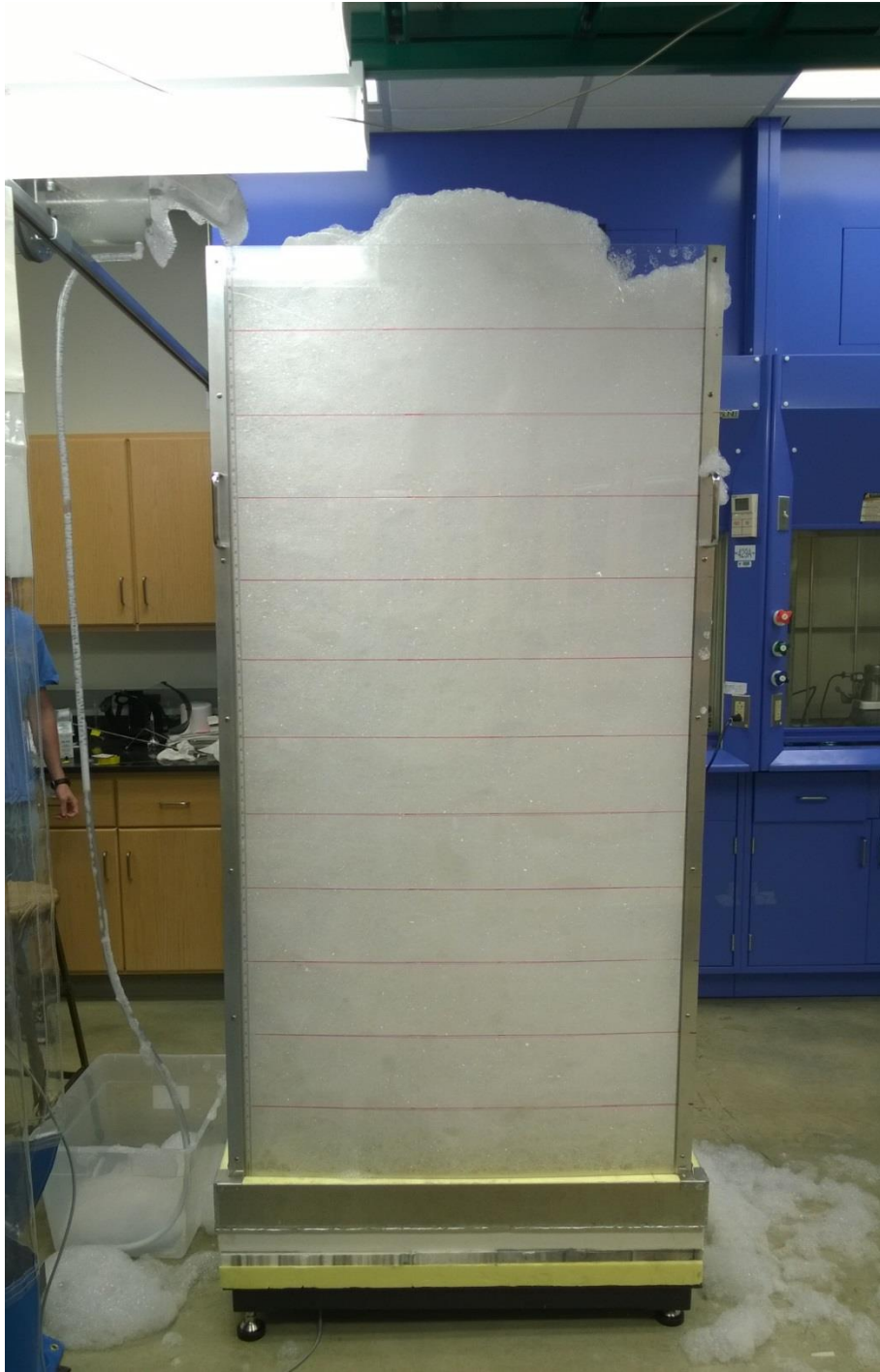


Figure 13. Foam container and fence full of high-expansion foam

3.3.1 *Expansion Ratio*

There are two main factors that contribute to changes in expansion ratio. These factors are the air flow rate and the liquid flow rate. The air flow rate can be adjusted by the damper, which is positioned behind the fan. The foam solution flow rate can be adjusted by the pressure regulator positioned directly after the pump. In order to measure the mass that is added to the foam collection container during foam application, the container is situated on a mass balance. In the expansion ratio calculation shown in Equation 1, the only unknown is the mass change during foam application. There are two other slight contributions to the mass in the container besides the mass of the foam solution. The first is the increased pressure of the air contained inside the foam bubbles. The second is the increased pressure of the air at the bottom of the container due to the gravitational effect of bubbles that are stacked above. Both of these effects are negligible compared to the mass of the foam solution, with an approximate contribution of 2.8 g as compared to the 2-4 kg contributed by the foam solution.

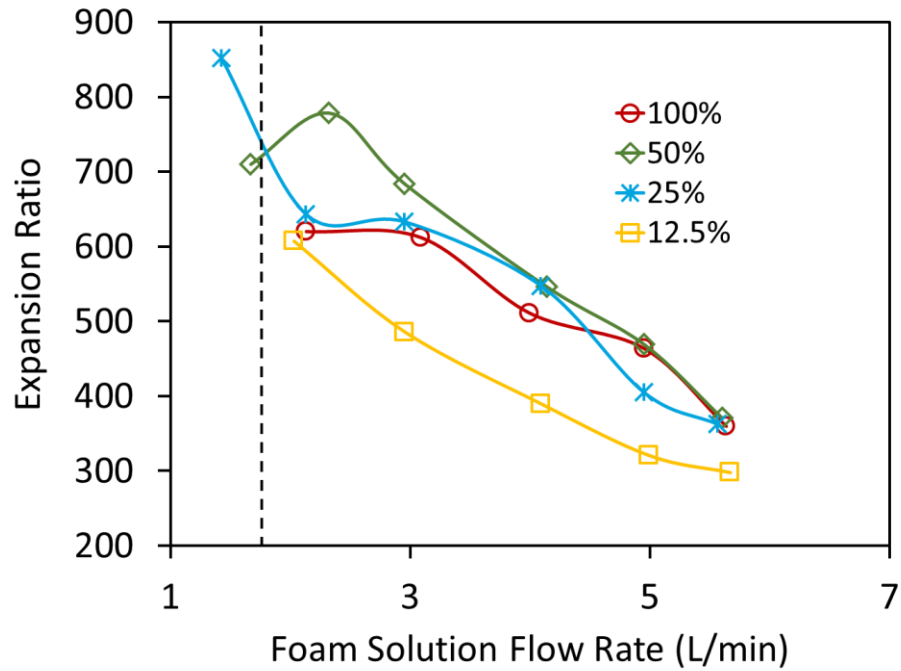


Figure 14. Expansion ratio vs. foam solution flow rate for all expansion foam trials. Values in the legend represent aperture position and are written as percentage of the area open to flow. Trials left of the vertical line were conducted using the smaller nozzle, all others were conducted using the larger nozzle

These trials were run with four different aperture settings (100%, 50%, 25%, and 12.5%) and five different pump settings (5, 10, 20, 30, and 40 psi). Although the independent variable controlling foam solution flow is actually pump pressure, the more representative variable is volumetric flow rate of the foam solution. Figure 14 shows the data for expansion ratio with changing foam solution flow rate and aperture position. The lowest expansion ratio of the trials is 298, which is well into the range of high-expansion foams (200+). The highest expansion ratio is 852, which is in line with many commercially available foam generators³⁹⁻⁴². The vertical dashed line represents the change from a small nozzle (BETE WL-1) to a large nozzle (BETE WL-1½)⁵⁰. Most of

the trials were conducted using the larger nozzle, and these trials are positioned to the right of the dashed line. The smaller nozzle was also used to try to examine the upper limits of expansion ration that the foam generator could produce.

For each damper position, increasing the foam solution flow rate decreases the expansion ratio. In a scenario where all of the air becomes entrained in the foam bubbles, the shape of the data would be an inverse-x curve. This relationship can be determined by rearranging the fundamental expansion ratio equation (Equation 2) as a function of only air and foam solution flow rates (Equation 3).

$$Exp. Ratio = \frac{V_{Foam}}{\left(M_{Foam Solution} / \rho_{Foam Solution} \right)}$$

Equation 2. Fundamental expansion ratio equation

$$Exp. Ratio = \dot{V}_{Air} * \frac{1}{\dot{V}_{Foam Solution}} + 1$$

Equation 3. Expansion ratio formula rearranged

In Figure 4, 12.5% open is the only damper position that can be approximated by an inverse-x. The rest of the damper positions seem to follow a more complex curve although all three stay fairly close together. The explanation for why increasing air flow does not increase expansion ratio as much as Equation 3 would predict is that lower amounts of air are entrained in the foam bubbles. Although not present in the expansion ratio data, visual observation of the trials supports this claim. In higher air flow trials, the

trajectory of the foam bubbles becomes straighter and more forceful, demonstrating the increase in the amount of air that escapes through the screen without forming foam.

One interesting finding at very low flow rates is the drop in performance for the 50% open aperture. For a majority of the trials, 50% aperture position performs the best; however, when the small nozzle is used, the 25% aperture creates foam with a higher expansion ratio. Further experiments were conducted to look into this behavior. These trials are shown below in Figure 15.

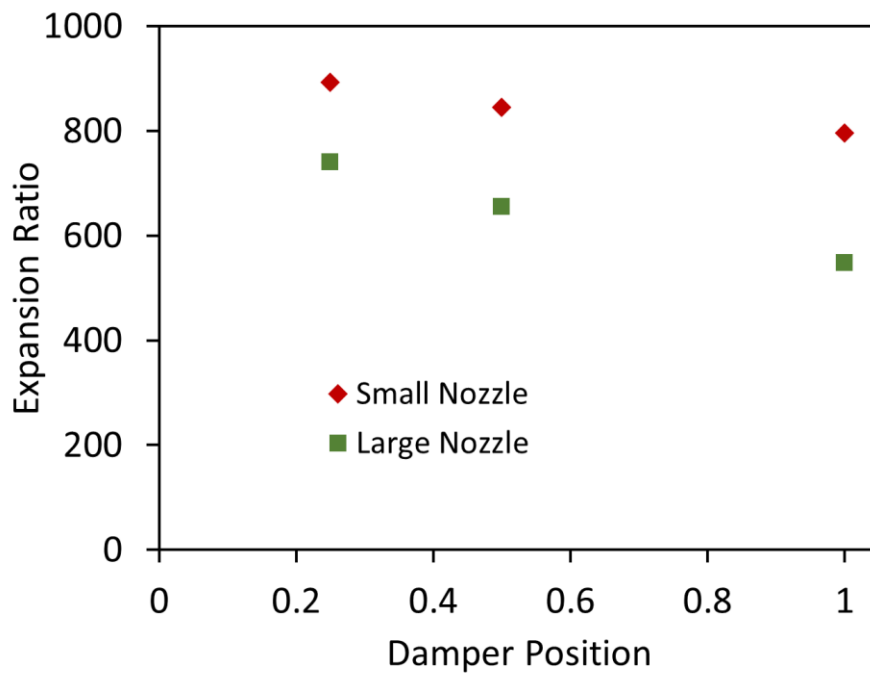


Figure 15. Comparison of expansion ratio at different damper positions using the small nozzle (WL1) and Big nozzle (WL1½) keeping foam solution flow rate constant

Trials were conducted to determine the effect of nozzle size and damper position when foam solution flow rate was very low. In all of these trials the foam solution flow

rate was held constant at 2.13 L/min. This liquid flow rate was chosen in an attempt to achieve the highest expansion ratio. Both the large and small nozzles follow the same trend; increasing air flow rate by opening the damper results in a lower expansion ratio. This trend is not present in the majority of the trials in Figure 14; however, it is present when using the small nozzle in trials left of the vertical dashed line. Although the data does not present a conclusion, visual observation of the trials is once again useful for these tests. When the foam solution flow rate is very low, the air can effectively carry the foam bubbles fairly far. At high air flow rates, which are present when the aperture is set at 50% and 100% open, the foam bubbles are carried forcefully into the back wall of the foam fence. This contact with the fence disrupts the stability of the foam matrix, causing it to rapidly break down and not have the same expansion ratio as foam that is gently applied into the container. With a lower air flow rate, which is present when the aperture is 25% open, the foam trajectory follows a more parabolic shape and does not make the same hard contact with the back wall of the fence. This appears to preserve the high expansion ratio of the foam bubbles, giving the highest expansion ratio of any of the trials.

Another important finding is the effect of nozzle size on expansion ratio. As mentioned before, the foam solution flow rate of all of the trials in Figure 15 were identical, meaning that changes in nozzle size should not have resulted in a change in expansion ratio. However, in each of the three pairs of trials, the small nozzle (BETE WL-1) outperformed the large nozzle (BETE WL-1½). The reason behind this increase in expansion ratio is tough to determine; however, one potential explanation is that at

low pressures, the nozzles spray patterns are not as reliable as they are at high pressures. In order to maintain equal foam solution flow rates, the large nozzle was operated at 5 psi, whereas the small nozzle was operated at 11.5 psi⁵⁰. BETE suggests operating the nozzles at pressures above 10 psi. Although differences in the spray pattern were not visible to the naked eye, it is likely that by operating at a pressure below the pressure the nozzle is rated for, the spray characteristics are sub-optimal.

3.3.2 *Time to Half-Height*

Typically the metric used to measure foam stability is “metric quarter time”⁵¹. Metric quarter time is defined as the time it takes for 25% of the foam solution contained in the foam to revert back to the liquid phase. This is typically measured by producing foam and containing it in a vessel with a drain valve as the bottom. The vessel is weighed before and after foam addition to determine initial mass of foam in the vessel. Over time, as the foam breaks down, liquid pools in the bottom of the vessel and drains into a beaker which is placed on a scale, measuring the mass of foam that has reverted back to the liquid phase. When the mass in the beaker is 25% of the original foam mass, the time is recorded as the metric quarter time. In the laboratory setup for these experiments an alternate measure of foam stability was used. This measurement is called “time to half-height” and is defined as the time it takes the foam blanket to collapse to half of the original application height.

In order to collect height information throughout the trial, all trials were filmed using a mounted video camera. For reference, the fence was marked with horizontal lines spanning its width. These lines were located beginning six inches below the top of

the fence and spaced six inches apart. For a majority of the trials, visual observation of the video was used to determine the time to half-height. In many trials, the foam did not collapse evenly, resulting in uneven foam height which could complicate half-height times. In these cases, the height at the center of the container was used.

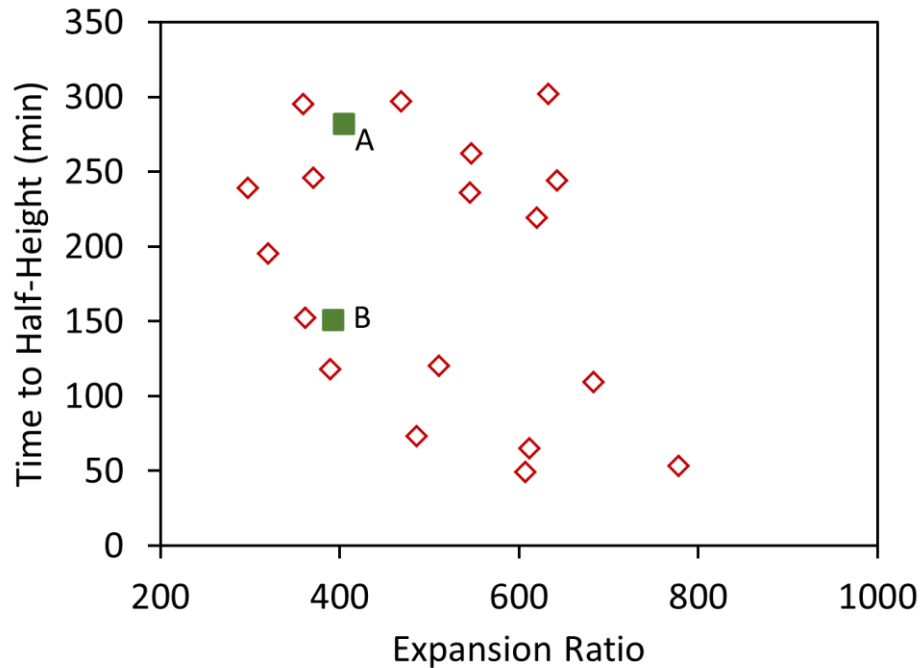


Figure 16. Time to half-height vs. expansion ratio for all large nozzle trials. Trials A and B have been highlighted to show the effect of foam solution age on time to half-height

Conroy *et al.*⁵¹ developed a model for the quarter drain time of high-expansion foams based on some of their characteristics such as expansion ratio and bubble size. In that work, higher expansion ratio is correlated with faster drainage rates. It was hypothesized that although this work uses a different stability criteria than quarter drain time, the model developed in Conroy's work should still be correlated to the stability

criteria used here, time to half-height. In stability experiments conducted in this work, there seems to be very little dependence on expansion ratio. One contributing factor is that the foam solution used in each trial was not handled in the same way. In early trials, batches of foam solution were mixed and often let sit for up to seven days or longer. This sitting time contributed to a decrease in the stability of the foam solution. Trials A and B, present as green boxes in Figure 16, highlight this issue. Both of these trials are conducted with a pump pressure of 30 psi and a damper position of 25% open. Additionally, their expansion ratios are almost identical. Trial A has an expansion ratio of 405 and Trial B has an expansion ratio of 393 (difference of 3%). The main difference in these trials is that Trial A uses foam solution that was mixed 28 hours before it was tested and Trial B uses foam that was mixed approximately 220 hours before it was tested. The resulting times to half-height were 282 minutes and 151 minutes respectively. This represents a decrease of more than 46%, dropping it from one of the more stable foams to slightly below average.

This behavior motivated follow up trials to measure the significance of allowing foam solution to sit in the foam solution tank before testing. The possible sources of loss in stability are time between mixing and testing and exposure to the air, pipework, and foam solution tank. Two batches of foam solution were mixed and tested to study this issue. The first was mixed and poured into the foam solution tank and allowed to stay in the tank throughout the trials. The second was mixed and left in a LDPE carboy with a sealed cap and only poured into the foam solution tank directly before use. The results from these trials are depicted below in Figure 17.

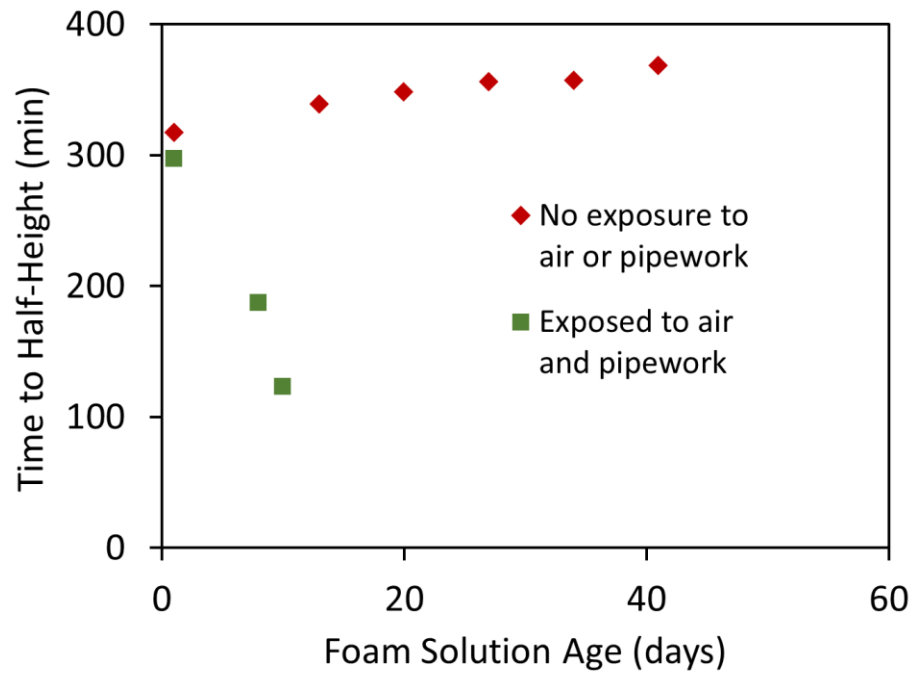


Figure 17. Time to half-height vs. foam solution age for exposed and unexposed scenarios

In trials where the foam solution is not exposed to air, pipework, and the foam solution tank, the foam shows no decrease in time to half-height with increased age, meaning that the drop in foam stability was likely due to interaction with air, pipework, or the foam solution tank and not simply due to aging. The second study was conducted with the foam solution left in the foam solution tank, which is not isolated from the air, and a significant drop in time to half-height occurred with foam solution older than eight days. This study served to eliminate the potential factor of foam solution interaction with the pipe work due to the offset time in between trials. The first trial (on day one) was run immediately, with no time spent in the pipework and no time spent exposed to air. The

second trial (at eight days) was run with seven days spent exposed to the pipework and seven days spent exposed to the air. The third trial (at 10 days) was run with two days spent exposed to the pipework and nine days spent exposed to the air. If pipework exposure was the determining factor in foam stability, then the time to half-height for the trial at 10 days would be expected to be higher than the time to half-height at eight days. From these trials, the conclusion can be made that exposure to air or the foam solution tank is the main contributor to a decrease in foam solution stability.

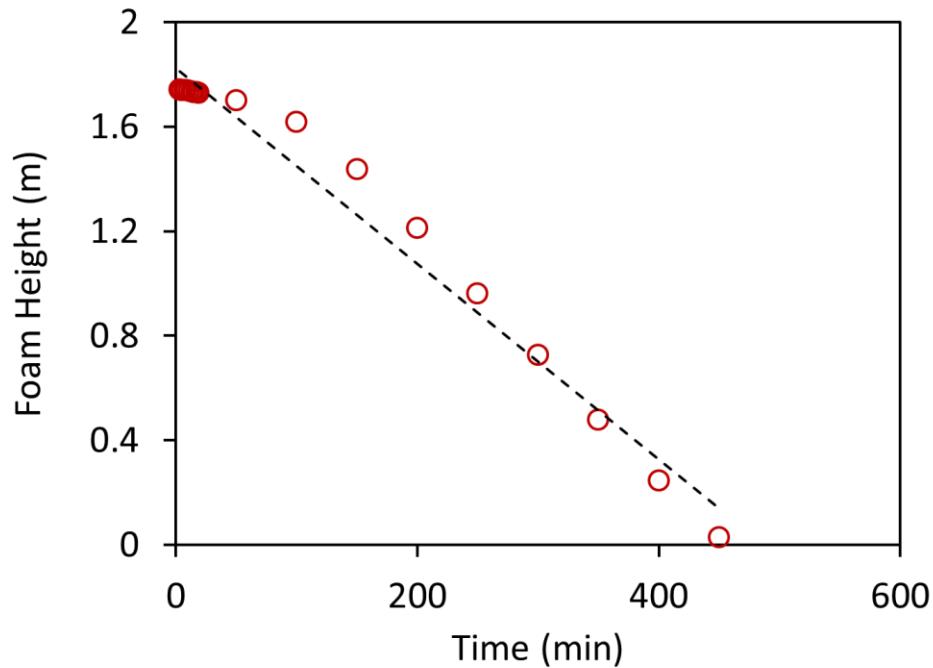


Figure 18. Foam breaking info for a full trial with a linear trend line for visual reference

Figure 18 shows the foam height throughout a single trial to illustrate how foam height changes with time. In this trial the pressure was 5 psi and the damper was set at 25% open, resulting in an expansion ratio of 643 and a time to half-height of 244

minutes. For the purposes of comparison, the linear fit predicts a time to half-height of 245.4 minutes. For this analysis, the video was broken into pictures at one minute intervals and MATLAB was used to analyze the position of the upper surface of the foam. From that information, foam height could be calculated accurately across the trial. As the figure demonstrates, there is a highly linear dependence of height on time, with an R^2 value of 0.978. This linearity is also present in other trials regardless of application conditions. The figure also shows the relatively slow initial breaking rate, which is described in the work by Conroy *et al.*⁵¹. The reason behind this behavior is that upon initial foam production, the foam is relatively “wet,” meaning that it has a high foam solution content. As the foam solution begins to drain out of the foam matrix, the foam height remains stable until it drains to a point where the foam bubbles can no longer support themselves and they collapse. This foam solution draining requires some time to occur, causing the foam height to remain nearly constant early in the trial.

3.3.3 *Foam Production Rate*

In addition to foam quality characterization such as expansion ratio and time to half-height, another important criterion of foam generation is foam application rate. The application time is the period between the moment the first bubble of foam entered the foam collection container to the moment the foam generator was unpowered, recorded by a video camera. The foam application rate is determined by dividing the total volume of the foam collection container by application time, the error of which is estimated to be within 4% due to a trivial part of foam spill out of the container.

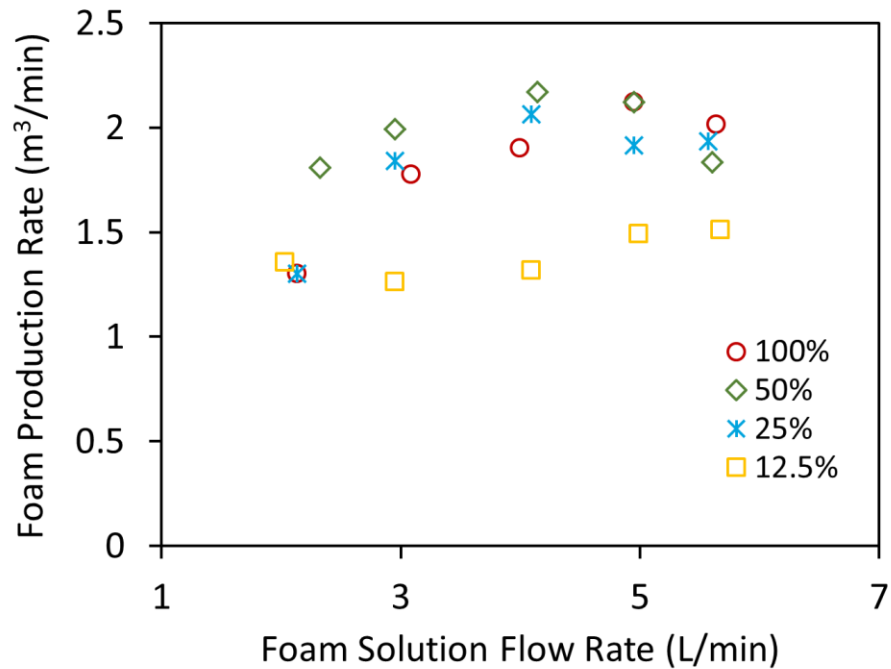


Figure 19. Foam production rate (m^3/min) for expansion foam tests. Only trials using the larger nozzle are depicted. Values in the legend represent aperture position and are written as percentage of the area open to flow.

Foam application rates for all of the trials were found to be between 1.2 and 2.2 m^3/min , which are well suited for lab-scale research purpose, compared with the high application rates of commercial generators (larger than 38 m^3/min). The foam production rate for the damper position at 12.5% open was much lower than the production rate at other damper settings because the air flow rate was the limiting factor in foam formation. The foam production rate is essentially a measure of how much air is trapped in foam bubbles and when the air flow rate drops below a threshold value, the foam production rate drops along with it. This same effect can be seen in the expansion ratio data in

Figure 14, where the limiting air flow rate caused a decrease in expansion ratio when compared to other damper settings.

3.4 Conclusions

The foam generating apparatus developed in this work was able to address all of the issues that exist with using an industrial-scale foam generator for lab use. The foam generator was able to produce high quality foams at flow rates that fit lab-scale research. These foams had expansion ratios between 298 and 892, with an average time to half-height around 185 minutes. The uncoupling of the air flow rate and the liquid flow rate also allows the researcher customizability without changing components of the generator, which is an advantage over industrial-scale foam generators. The portability and availability of the equipment, lack of water discharge at the beginning of a trial, and lower cost of building equipment are also advantages to the researcher that this equipment can offer. The constructed generator also exhibited good customizability, allowing the researcher to substitute many of the parts in order to create a foam with a variety of different physical characteristics. The main variables that were adjusted were foam solution pressure, damper position, and nozzle size, each of which showed a strong effect on the resulting foam. In addition to these variables, many other adjustments can be made to produce a desirable, applicable foam.

4. DECONTAMINATION

4.1 Selection Of Decontamination Foam Formulation

Before beginning any experiments, a suitable decontaminant had to be selected. Although there are decontamination foams on the market, the contents of the foam are trade secrets, and their recipes are undisclosed¹⁷. There is a decontamination solution, developed by the military, called Decon Green. This solution was developed with a focus on keeping the foam non-toxic and environmentally safe. When the solution was developed, components were selected that were safe for human contact, and in many cases safe for human consumption. Additionally, only ingredients that were environmentally friendly were used⁵². The main components of Decon Green are hydrogen peroxide, propylene glycol, potassium citrate, potassium molybdate, potassium bicarbonate, propylene carbonate, and Triton X-100. Hydrogen peroxide can be used as a disinfectant at low concentrations (3%). Propylene glycol, potassium citrate, potassium molybdate, and potassium bicarbonate are all used in foods, supplements, or medicines. Propylene carbonate is used in cosmetics. Triton X-100 is not approved for human use, but is an agricultural surfactant and is bio-degradable⁵². Although hydrogen peroxide is used in much higher concentrations in Decon Green than the amount approved for human use (10% vs 3%), it provides an increase in decontamination effectiveness, which is viewed as an acceptable tradeoff. The detailed recipe of this foam is provided below

Table 3. Decon Green recipe ⁴

Ingredient	Volume Percent
Propylene Carbonate	60
35% Hydrogen Peroxide	30
Triton X-100	10
Potassium Carbonate	2.07g/100mL
Potassium Molybdate	0.48g/100mL

This solution is well suited to research because the formulation is public; the solution is non-toxic, non-flammable, non-corrosive, and environmentally friendly; and the components can all be purchased for use in the lab. In knowing the ingredients of the solution, there exists an increased ability to customize the foam for personal use.

4.2 Development of Decontamination Foam

Beginning with the Decon Green recipe, changes were made to convert the decontamination solution into a decontamination foam. Although Decon Green contains, a liquid and a surfactant and is therefore possible to create a foam, in experiments the foam matrix was not forming. A variety of solutions were created to determine which components were preventing foam formation. A summary of these solutions is presented below in Table 4.

Table 4. Developing decon foam formulation

Solvent	Surfactant	H ₂ O ₂	Potassium Manganate	Potassium Carbonate	Foam Height	Collapse Time
Propylene	Triton X-100	Yes	No	No	½"	seconds
Water	Triton X-100	Yes	No	No	Full	2 hours
Water	HE	Yes	No	No	Full	10 hours
Propylene	HE	Yes	No	No	¼"	seconds
Propylene	Triton X-100	Yes	Yes	No	¾"	seconds
Water	Triton X-100	Yes	Yes	No	Full	2 hours
Water	HE	Yes	Yes	No	Full	8 hours
Propylene	HE	Yes	Yes	No	½"	seconds
Water	Triton X-100	No	Yes	No	Full	2 hours
Water	Triton X-100	No	No	No	Full	1.5 hours
Water	HE	No	No	No	Full	10 hours
Water	HE	No	No	No	Full	10 hours

Some of the components that were contributing to an unstable foam matrix were propylene carbonate, potassium carbonate, and Triton X-100. These compounds were substituted or removed in order to create a foam that was suitable for use in the lab. In Table 4, the column that is highlighted in green shows the materials that were used in the final formulation.

The first change was to substitute propylene carbonate for water. Propylene carbonate is a non-protic polar solvent which has a very low melting point making it useful in conditions where water would freeze⁵³. Propylene carbonate does not readily form foams, as was seen in early experiments conducted in the lab. For this reason, water was chosen as the main solvent. Because both water and propylene carbonate are polar solvents, this change can be made without affecting the solubility of other components.

The next change was in the selection of surfactant. In the Decon Green recipe Triton X-100 is used as the surfactant; however, it does not provide the same long-term stability as other high-expansion foam surfactants. For this reason it was substituted with C2 High Ex Foam (HE) from Tyco fire protection products. In the original formulation, Triton X-100 is present as 10% of the total volume; however, due to the increased stability of HE, this proportion was decreased. The manufacturer recommendation for HE proportion is 2%; however, stability trials determined that this proportion was too low to give the foam the long term stability that was desired. The proportion was increased to 4% which gives good long-term stability, while keeping the surface tension high enough that the foam can be created with a relatively low expansion ratio.

Another change was to remove potassium carbonate from the solution. Potassium carbonate is used as a pH adjustor, which can be useful depending on the application of the decontamination solution; however, it causes disruption in the foam structure which decreases the stability significantly. For this reason, the potassium carbonate was removed from the final foam composition, which is shown below in Table 5.

During experiments, potassium molybdate was also removed from the foam formulation in order to simplify the formula. In the work by Wagner *et al.*⁵², the molybdate ion was used to catalyze the oxidation of HD, which has a sulfide group; however, molybdate catalysis of thiol oxidation has not been documented in literature. It is possible that inclusion of the potassium molybdate would improve decontamination; however, in order to keep the formulation as simple as possible it was removed.

Table 5. Decontamination foam recipe

Ingredient	Volume Percent
Deionized Water	66
30% Hydrogen Peroxide	30
C2 High Ex Foam	4

5. LIQUID PHASE DECONTAMINATION

5.1 Introduction

As mentioned previously, although decontamination work has been conducted, the focus has been mainly on the development of decontamination solutions and foams for chemical and biological warfare agents as opposed to industrial spill decontamination. Among these studies, the efforts mainly focused on neutralizing polar hazardous chemicals and the tests on non-polar contaminants did not explain the underlying dissolution issues. In addition, the performance of decon foam has never been compared directly with that of decon solution.

This work selected a variant of cysteine as the contaminant, which is representative of industrial bio-chemicals. This compound is able to dissolve in a water-based foam solution, but has a fairly low solubility and low dissolution rate, allowing non-polar decontamination to be addressed. Additionally, this work compares decon solutions with and without surfactant directly as opposed to comparing decon solution with decon foam. By comparing the decontamination foam solution (DFS) to decontamination solution without foam (DS), the effect of surfactant can be studied.

5.2 Materials and Methods

5.2.1 Contaminant

The chosen contaminant was N-(tert-Butoxycarbonyl)-L-cysteine methyl ester (abbreviated TCME), which is a protected derivative of cysteine. Cysteine is an amino acid with a thiol side chain. This sulfur group allows cysteine to be used as an analog for a variety of industrial contaminants that contain sulfur, and its oxidation has been well

documented in literature ^{5,23-25,54-56}. However, cysteine is difficult to analyze using GC-MS due to its high polarity and subsequent high melting and boiling points ⁵⁷⁻⁶⁰. In order to reduce the polarity of the cysteine molecule, a protected derivative was used. This derivative has side groups on both the carboxylic acid and amine groups, but leaves the thiol exposed, allowing a similar nucleophilic oxidation reaction to occur. The TCME has a two part benefit of being easier to analyze using GC-MS as well as allowing the study of non-polar decontamination. The TCME was purchased from Sigma Aldrich and had a purity of >97%. This purity was verified through GC-MS analysis.

5.2.2 *Decontamination Solution Preparation*

The two types of decontamination technologies tested in this work were DS and DFS. The DS was made by mixing 70 volume percent deionized water and 30 volume percent 30% hydrogen peroxide (H₂O₂) in water in 10 mL batches. The DFS was formulated by mixing 66 volume percent deionized water, 30 volume percent 30% H₂O₂ in water, and 4 volume percent high-expansion foam concentrate, following a similar recipe of Decon Green, a decontamination solution developed by the military ⁵². Both solutions contained water with H₂O₂; however, DFS also include high-expansion foam concentrate. The concentrate used was C2 High Ex Foam (HE) from Tyco fire protection products. In the solutions, water functions as the solvent, H₂O₂ is the active component for oxidizing the contaminants, and HE is the surfactant responsible for creating the foam.

5.2.3 Decontamination Reaction

All experiments were conducted in 10 mL glass vials. TCME was injected into the vials using a micropipette, in amounts shown in Table 6. Trials without incubation time utilized the full spectrum of TCME concentrations; however, trials with incubation time were conducted using the medium-low injection volume (5 μ L). Following this, 1 mL of decontamination solution and 0.5 mL of water were injected. The vials were then capped and manually shaken for 30 seconds and allowed to sit for the allotted time. All reactions were conducted at room temperature.

Table 6. Experimental variables

Hold Time (min)	Reaction Time (min)	TCME Injection Volume (μ L)	Decon Technology
0	20	30 (high)	DS
20	120	10 (medium-high)	DFS
120	300	5 (medium-low)	
300	1440	1 (low)	
1440			
2520			

The decontamination reaction occurs between the H_2O_2 and the exposed thiol group. The reaction is not well understood, but it is assumed to be similar to the well documented oxidization of cysteine as follows, due to the analogy in the molecular structure between TCME and cysteine. In the base state, the sulfur atom of cysteine is bonded to a hydrogen atom. As the oxidation reaction of cysteine progresses, the sulfur loses its hydrogen and bonds to the sulfur of another cysteine molecule, forming a dimer called cystine. Cystine is insoluble; however, if the dimer was kept in solution by decreasing the pH, then the sulfur would continue to oxidize forming cysteine sulfinic

acid and finally cysteic acid. All of these reactions occur in the aqueous phase due to the polarity of H₂O₂ and the reaction medium, which is water or foam solution (96% water).

5.2.4 GC Sample Preparation

Samples were prepared by pipetting 100 µL of reaction liquid into 1 mL of dichloromethane (DCM). In samples with high TCME concentration or with low dissolution time, some TCME remained on the bottom of the glass vials. Care was taken to ensure that the 100 µL aliquot was drawn from the bulk solution not from the separate TCME phase. When the samples were injected into the DCM, the reaction products were present in the aqueous phase; in order to extract them into the DCM more rapidly, the samples were agitated. After agitation the samples were allowed to rest for 15 minutes and 500 µL of the DCM solution were pipetted into the GC autosampler vials for analysis.

5.2.5 Analytical Methods

Each sample was analyzed using an Agilent 7890B GC coupled with an Agilent 5977A mass selective detector. The method for these trials used an injection temperature of 250°C, an initial temperature of 45°C held for 3 minutes, a final temperature of 320°C held for 5 minutes, and a ramp of 20°C per minute over 13.75 minutes. The carrier gas was UHP (5.0) helium (Praxair) with a pressure of 23.5 psi and a flow rate of 306 mL/min and the split ratio was 100:1. The column was a HP-5MS (30 m x 0.25 mm i.d., 0.25 µm film thickness). The mass spectrometer was operated in full scan mode (50-550 amu) to identify all possible TCME oxidation products. The GC was calibrated

using a series of standard solutions of TCME dissolved in dichloromethane to determine the relationship between peak area and TCME concentration.

5.3 Results and Discussion

Due to the infrequency with which TCME is used, there were some important characteristics of the chemical that were not available; the mass spectrum of TCME for MS analysis, the solubility of TCME in water, and the solubility of the TCME dimer in water or in DCM. Although the NIST library of compounds did not contain the chemical, the library contained very similar chemicals which could be used for comparison. Multiple standards were run through the MS to confirm the atomic mass units and intensities of the peaks for future confirmation of the existence of TCME. The 10 most common peaks and an example spectrum are shown below.

Table 7. Mass spectrum information for pure TCME dissolved in DCM

Peak (amu)	57	118	59	76	88	179	186	162	120	134
Abundance	999	666	321	320	258	212	186	137	126	92
Standard Deviation	0	56	32	20	21	18	9	14	12	6

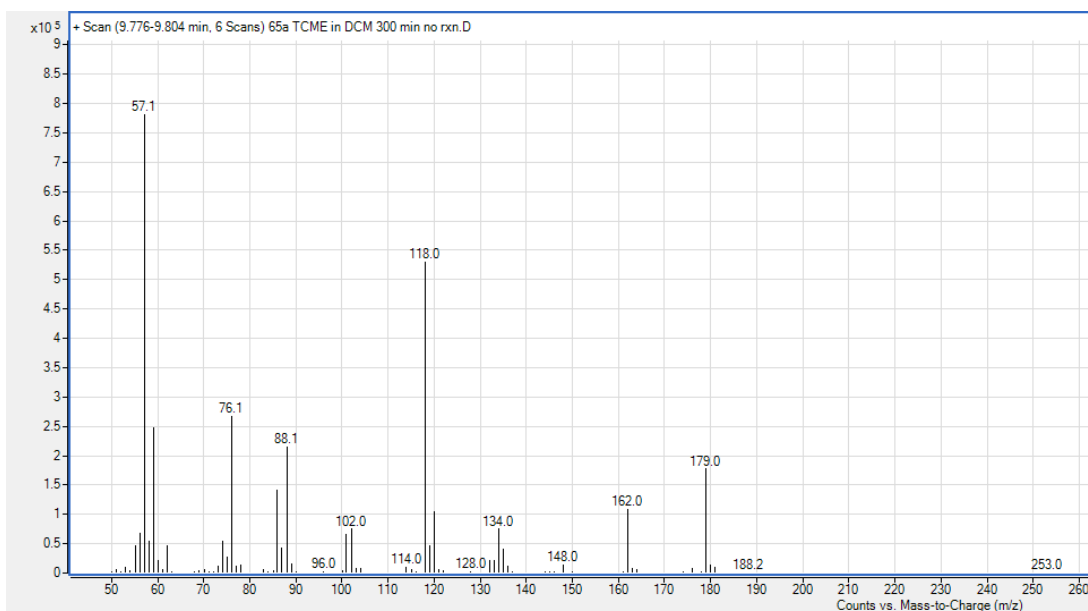


Figure 20. Mass spectrum of TCME dissolved in DCM

As mentioned previously, the solubility of TCME dimer is not published; however, it did not appear during GC-MS analysis, probably due to the insolubility of TCME dimer. Otherwise, the polarity of the thiol group will promote the dissolution of the sample and the peak will appear in the GC chromatograms, which are shown in Figures 21 a-d.

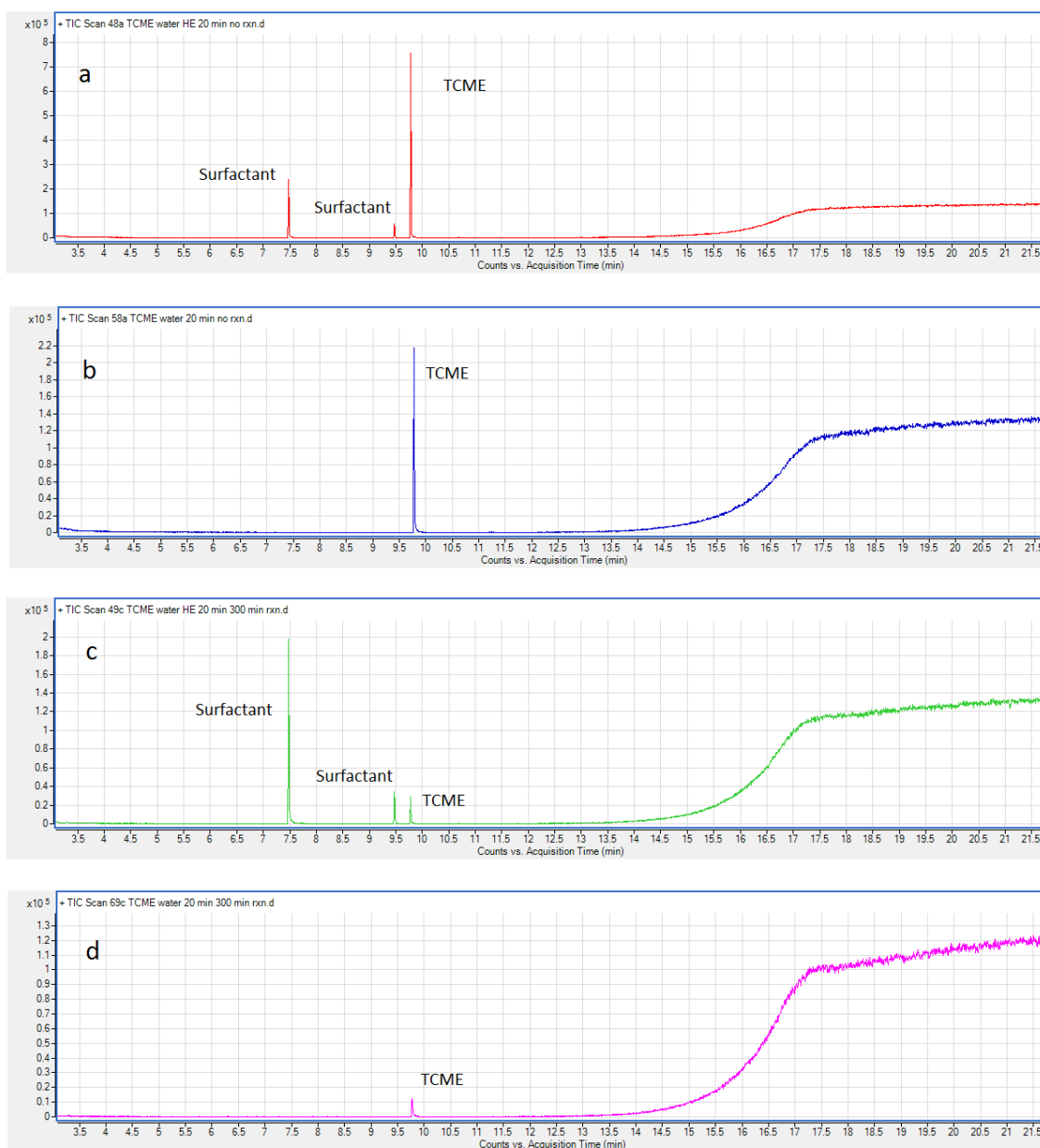


Figure 21. Chromatograms of four different GC trials; (a) TCME dissolved in FS with 20 minute incubation and no reaction, (b) TCME dissolved in water with 20 minute incubation and no reaction, (c) TCME dissolved in DFS with 20 minute incubation and 300 minute reaction, (d) TCME dissolved in DS with 20 minute incubation and 300 minute reaction.

Figures 21 a and b show the TCME dissolved in FS and water respectively. The peaks present at 7.5 minutes and 9.5 minutes are 2-2 ethanol-(butoxyethoxy) and 1-dodecanol, both of which are compounds in the surfactant. The peak present at 9.77 minutes is the TCME. When H₂O₂ is introduced, the TCME peak drops significantly, as shown in Figures 21 c and d; however, the surfactant peaks remain at their original levels because they do not participate in the reaction. It is also clear that no new peak is formed during the reaction, meaning that the TCME dimer is either insoluble in the aqueous phase or in the dichloromethane. The assumption of dimer precipitation is also verified by the existence of a white precipitate in the bottom of the sample vials, which is similar to the precipitation of cysteine dimer during the oxidation reaction. Although the dimer cannot be detected by the GC-MS, the extent of reaction can be determined by measuring the difference between the initial concentration and final concentration of TCME. A similar approach was also applied in previous research by Love *et al.* ⁴, Wagner *et al.* ⁵², and Cronic ⁸.

Reaction time was controlled for four different periods: 20 minutes, 2 hours, 5 hours, and 24 hours. Due to the low solubility of TCME in the aqueous phase, some trials were conducted with an incubation time prior to the introduction of H₂O₂. In these cases, the TCME was allowed to dissolve in either water or water and HE, and after a predetermined amount of time, H₂O₂ was injected in order to initiate the reaction. In realistic application, delayed introduction of H₂O₂ cannot be achieved in the foam phase because spraying H₂O₂ on the foam matrix would firstly disrupt the foam, causing rapid collapse, and secondly would not distribute well throughout the foam, leaving sections

unreacted. Therefore, an alternative approach can be used. Initially, expansion foam that does not contain H₂O₂ can be applied to the affected area. When the foam contacts contaminants, it absorbs them and as it collapses it carries the contaminants with it. After complete collapse, H₂O₂ can be applied to the liquid pool, at which time oxidation of the contaminants will occur.

5.3.1 Baseline Decontamination Test Results without Incubation Time

Decontamination trials were conducted without incubation time to determine the oxidizing effect of H₂O₂ on TCME. Table 8 shows the volume of TCME injected in each vial and the final concentration based on the experimental procedure assuming complete dissolution. This can be compared to the concentration data obtained from the GC-MS, which is shown in Figures 22 and 23.

Table 8. TCME content for trials without incubation time

TCME amount	Volume (μL)	Mass (μg)	Concentration after dilution (μg/mL)
High	30	34290	2072
Medium-High	10	11430	690
Medium-Low	5	5720	346
Low	1	1140	70

TCME solubility is not documented in literature; however, trials were run to determine the solubility in both water and foam solution. The saturation point was determined to be 966 μg/mL with a standard deviation of 196 μg/mL in water and

1245 $\mu\text{g/mL}$ with a standard deviation of 306 $\mu\text{g/mL}$ in foam solution. In Figures 22 and 23 the maximum concentrations present in the “high” sample are very close to the saturation points, even though the dissolution time is relatively short. Dissolution occurring more rapidly than expected is likely due to an increase in solution temperature during decontamination reaction. The TCME decontamination reaction is exothermic, releasing heat as it progresses. Although the reaction happens slowly due to the transport limitations of the system, even small changes in solution temperature can have an effect on solubility limits.

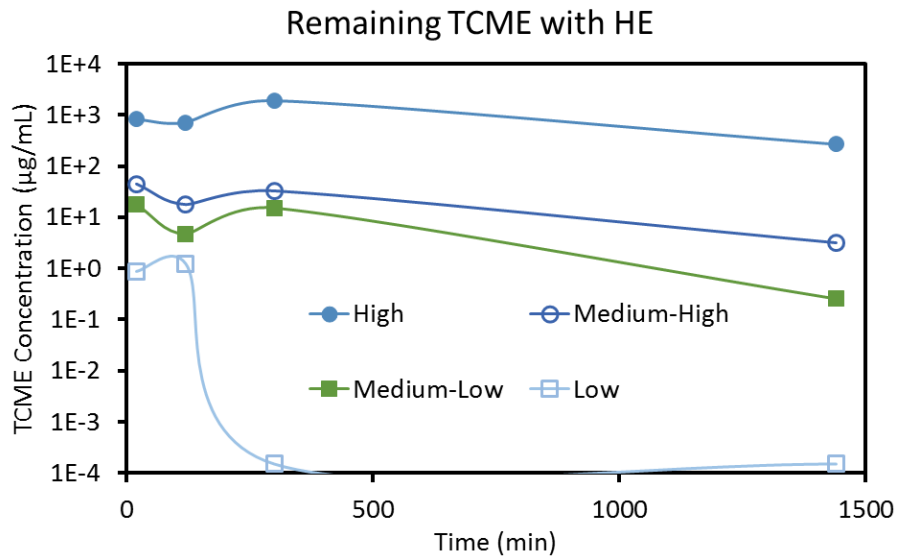


Figure 22. TCME concentration remaining in decontamination foam solution at reaction times of 20, 120, 300, and 1440 minutes changing initial injection volume of TCME

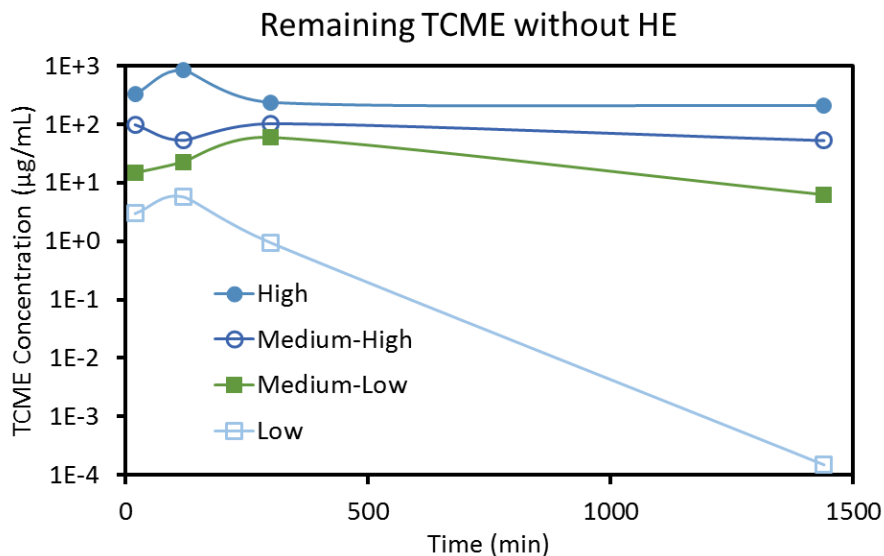
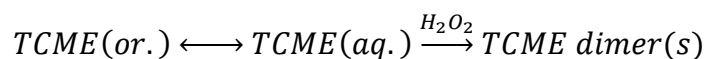


Figure 23. TCME concentration remaining in decontamination solution without HE at reaction times of 20, 120, 300, and 1440 minutes changing initial injection volume of TCME

Figures 22 and 23 show the TCME content vs. time for trials at high, medium-high, medium-low, and low concentrations. In all of these trials, the TCME content does not follow the expected trend of monotonic decrease with time. Instead it has an increase at some point in the trial, and in some cases this increase brings it above the concentration measured at 20 minutes. This behavior is likely due to the low solubility of TCME in water. Initially, the TCME and decon foam are in separate phases. As the TCME dissolves in the foam, it reacts with H_2O_2 in the reaction shown in Equation 1. Although the net quantity of TCME is decreasing as it reacts, because the GC is only able to detect the aqueous concentration of TCME, the relationship with time is more difficult to forecast. The dissolution step works to increase TCME in the aqueous phase, while the decontamination step works to decrease it. In the early part of the trials, the

TCME is dissolving rapidly because the concentration is low; however, it is also reacting rapidly because the H₂O₂ concentration is high. The H₂O₂ concentration decreases over time as a result of both the decontamination reaction and the decomposition of H₂O₂. H₂O₂ will naturally decompose over time to oxygen and water, decreasing the concentration available for reaction. As the TCME reacts, there is less present in solution, allowing the TCME to continue dissolving at approximately the same rate. The reason the TCME does not completely disappear, even at long reaction time, is due to the disappearance of H₂O₂. Although the H₂O₂ was initially present in excess, it is gradually consumed by both decontamination and decomposition. When H₂O₂ is completely consumed, TCME will no longer participate in the oxidation reaction.



Equation 4. TCME reaction pathway

5.3.2 TCME Solubility Tests with Incubation Time

In order to address the issue of unexpected increases in TCME content, an incubation time was introduced. The incubation time provided an opportunity for the TCME to dissolve in the water or foam solution (FS) before the introduction of H₂O₂. In order to measure the effect of time on dissolution, trials were conducted without H₂O₂ and the TCME concentration was measured. Additionally, TCME content was fixed at 5 μL for the remainder of the trials. This value was chosen because it is below the saturation point of TCME in water at room-temperature. Conducting trials below the

saturation point is important because over-saturated solutions will not reflect changes in concentration as the reaction proceeds. Standard solutions with incubation time with and without HE are shown in Figure 24. The data follow each other fairly closely, meaning that the surfactant does not have a strong influence on TCME solubility.

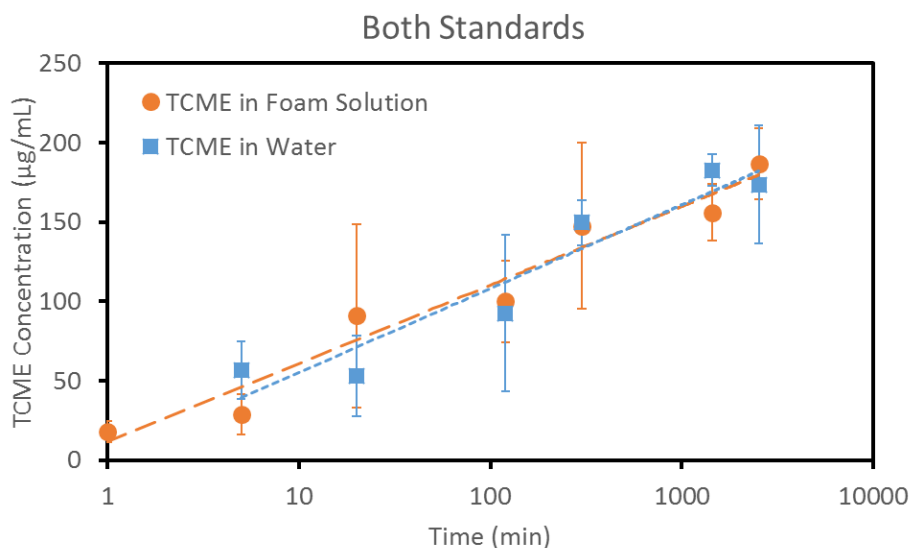


Figure 24. Comparison of TCME solubility in solutions with and without HE changing incubation time. Both trendlines are logarithmic fits with the long dashes and short dashes fitting the foam solution and water data points, respectively.

The standards follow the dissolution rate predicted by the Noyes-Whitney equation, shown in Equation 5⁶¹. In this equation initial dissolution rate is constant; however, as the concentration in solution approaches saturation, the concentration plateaus. Because this solute/solvent system has a very low solubility, it approximately follows a logarithmic fit. Initially, the TCME concentration is very low, causing rapid dissolution to occur. As time progresses, the amount of TCME remaining out of solution

decreases and TCME concentration increases, both of which contribute to a slowing rate of dissolution. At extremely long times, either the TCME saturates the solution or all of the TCME is dissolved. The concentration with complete dissolution is 346 µg/mL, shown in Table 8; however, after 24 hours, the concentrations in both water and FS remain below that concentration, further illustrating the low solubility of TCME in polar solvents. In the case of these standards, the TCME will completely dissolve; however, at higher concentrations the TCME will saturate the solution and some will remain in a separate phase.

$$\frac{dW}{dt} = \frac{DA(C_s - C)}{L}$$

Equation 5. The Noyes-Whitney equation which describes dissolution. dW/dt is the dissolution rate, D is the diffusion coefficient, A is the surface area of the TCME, C_s is the concentration of TCME in the diffusion layer, C is the concentration in the bulk liquid, and L is the diffusion layer thickness.

5.3.3 Decontamination Tests

Figures 25 a and b and 26 a and b illustrate the importance of incubation time. When the TCME is given time to dissolve in the solution, it achieves much faster decontamination. In the shorter trials (1 and 20 minutes for DFS and 1, 20, and 120 minutes for DS), the TCME content did not achieve 99.9% decontamination even after a 24 hour reaction period with an H_2O_2 concentration that is in excess about 250-fold. This can be attributed to decomposition of the H_2O_2 . In trials where incubation time was

higher, the solution was more prepared for decontamination and the H₂O₂ was able to immediately react with TCME prior to its decomposition.

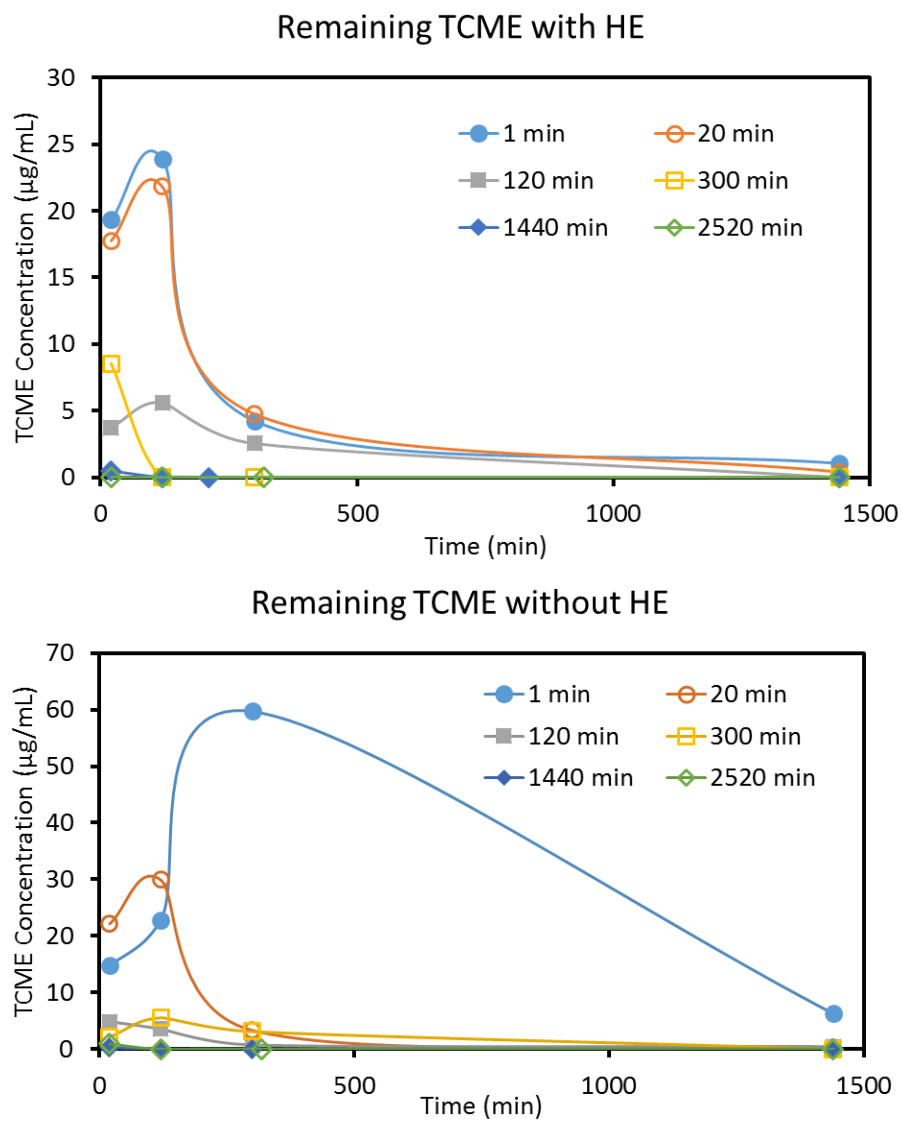


Figure 25 (a) TCME concentration remaining in decontamination foam solution at reaction times of 20, 120, 300, and 1440 minutes changing incubation time, (b) TCME concentration remaining in decontamination solution without HE at reaction times of 20, 120, 300, and 1440 minutes changing incubation time.

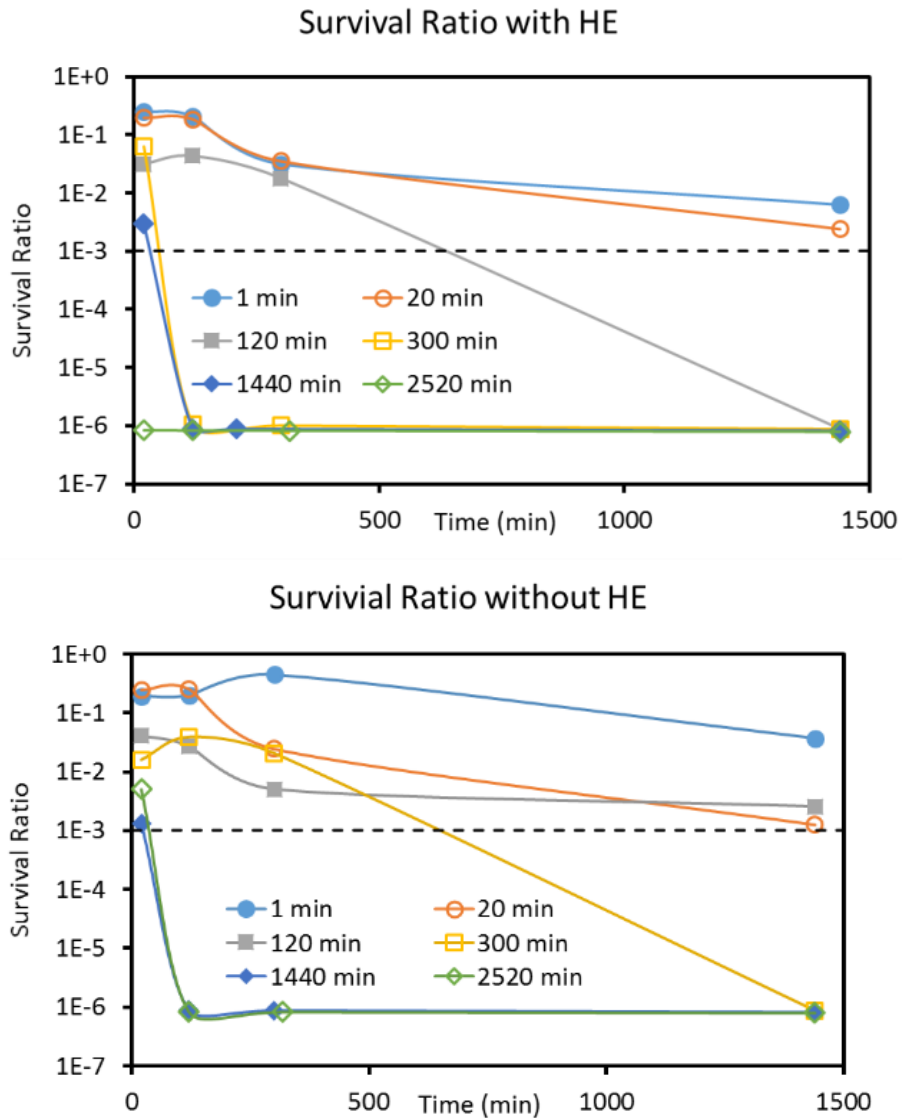


Figure 26 (a) ratio of TCME concentration remaining in solution to expected TCME concentration in DFS at reaction times of 20, 120, 300, and 1440 minutes changing incubation time (b) ratio of TCME concentration remaining in solution to expected TCME concentration in DFS at reaction times of 20, 120, 300, and 1440 minutes changing incubation time

$$Survival\ Ratio = \frac{TCME\ concentration\ in\ DS\ or\ DFS\ at\ time\ t}{TCME\ concentration\ in\ standard\ solution\ at\ time\ t}$$

Equation 6. Survival ratio of TCME in decontamination technologies

Figure 26 a and b show the survival ratio of the TCME when normalized by expected TCME concentration, shown in Equation 6. The expected TCME concentration is the concentration at time t with no reaction, which is the fit generated from the standards in Figure 24. There are three main characteristics of Figure 26. The first is the concentration at the first time point, the second is the overall shape of the curves, and the third is the concentration at the last time point. In general, as incubation time increased, the concentration at the first time point decreased. This occurs despite the fact that the amount of TCME that has dissolved in the aqueous phase increases as incubation time increases, shown in Table 9. This phenomenon can be attributed to the rapid reaction with H_2O_2 early in the trial when H_2O_2 concentration was highest. The shape of the curves show both the rapid decontamination at high incubation times and the slower decontamination at low incubation times. For DFS, trials with incubation times 300 minutes or longer achieved 100% decontamination by the second data point, which was taken at 120 minutes. For DS, the behavior was similar; however, the incubation time had to be increased to 1440 minutes or longer to achieve 100% decontamination after 120 minutes. Shorter incubation times did not follow this trend, and each of these samples remained above 99% decontamination even after 300 minutes. Despite the slow reaction, it is important to note that the spikes observed in Figure 25 are not present in Figure 26 because the increased dissolution is accounted for by dividing by the expected concentration. The last important characteristic is the final data point at 1440 minutes. Although all trials contain the same amount of TCME and H_2O_2 , if the TCME is not

available for reaction early in the trials it will persist due to H₂O₂ decomposition, resulting in remaining TCME at long reaction times.

Table 9. Initial concentration of DFS and DS trials at different incubation times

Incubation Time (min)	Decon Foam Solution Conc. (µg/mL)	Decon Solution Conc. (µg/mL)
1	25.5	10.3
20	76.4	66.5
120	114	108
300	134	130
1440	168	167
2520	180	181

Overall, decontamination trials in DFS and DS behaved very similarly with some small but important differences. This was expected due to the similar dissolution behavior of TCME in decon solutions with and without HE. In Figure 25, DFS trials with incubation times 120 minutes or longer reached complete decontamination, whereas in DS trials, the 120 minute incubation time did not reach complete decontamination. In Figure 26, DFS trials showed a general monotonic decrease throughout the trials; however, in DS trials, there were increases in survival ratio in some cases. Because the dissolution properties of both solutions were determined to be similar (Figure 24), there are likely differences in the reaction which may be attributed to the presence of HE.

5.4 Conclusions

Decontamination foam has mainly been studied for use against contaminants which can easily dissolve in foam; however, solubility issues play an important role in decontamination effectiveness. By allowing the contaminants time to dissolve in the foam before hydrogen peroxide application, decontamination can be even more effective. If this approach is not feasible, hydrogen peroxide stabilization may be a suitable alternative to preserve the effectiveness of H₂O₂ until the contaminant has had time to fully dissolve.

Although foam surfactant does not have a strong influence on TCME solubility, it does have an effect on extent of reaction. This phenomenon has not been studied further; however, future work in this area could provide valuable insight into the mechanisms that make decontamination foam effective in both military and industrial settings.

6. DECONTAMINATION USING FOAM GENERATOR

6.1 Introduction

As mentioned previously, decontamination foam is created by mixing DFS with air to form a semi-stable matrix of air trapped in liquid bubbles. This mixing can be done in two ways, either manually or with a foam generator. Manual mixing is effective for small-scale application, and can create foams of fairly low expansion ratios; however, creating higher expansion ratio foams is difficult because sustained mixing damages the foam structure. In order to achieve high foam application rates with higher expansion ratios, a foam generator must be used. Due to the large spill sizes which occur in industry, manual mixing is not a feasible approach, meaning that a foam generator is required.

In previous work, such as that done by Love *et al.*⁴, a thorough review and analysis of decontamination technologies was conducted using manual application of the foam. Although this can be effective, application using a foam generator would be more analogous to actual industrial foam application. This work uses a novel lab-scale foam generator that was originally developed and constructed by Harding *et al.*⁶², and is highly customizable, allowing the researcher great control over the foam properties.

6.2 Materials and Methods

6.2.1 Description of Decontamination Setup

The test apparatus used in the decontamination trials was the same as the apparatus used in the expansion foam trials, shown in Figure 9. Because decontamination foams are generally applied with a low or medium expansion ratio, the

pressure and damper parameters were altered to create foams with expansion ratios in the range of 20 to 75.

One major change was the container into which the foam was deposited. For the original high-expansion foam trials, the foam container was very large (about 2 m³). For decontamination foam trials, the expansion ratio was much lower, therefore the volume requirements for the foam container were much lower (from this point forward it will be referred to as decontamination foam container). Additionally the decon foam container required somewhere to apply the contaminant to conduct the decontamination reaction. A 56 L HDPE high density polyethylene (HDPE) box was used to create the decon foam container. The cysteine was applied to slides which are placed on six slide mounts prior to foam application. Six LDPE blocks were machined into foam trays which can contain any foam that drips off the slides. These slide trays and slide mounts are fastened to the walls of the decon foam container. The decontamination foam container and slide cradles are shown in Figure 27. Slide cradles, shown in detail in Figure 28 are mounted to the side of the container and contaminated slides are placed on the tray supports. When this process is complete, foam is applied using a lab-scale decontamination foam generator.

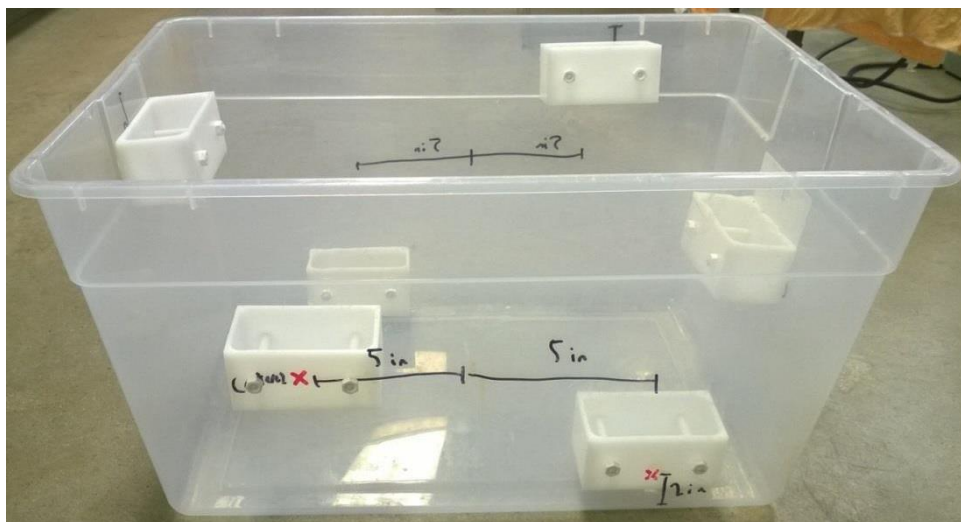


Figure 27. 56 L HDPE container showing the relative position and size of slide cradles

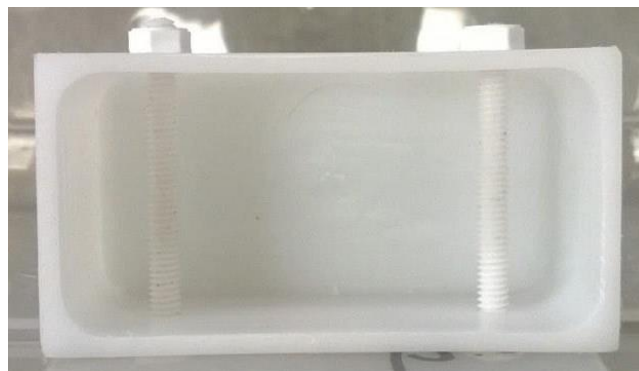


Figure 28. Close-up view of the slide cradle showing the bolts on which the slide is placed

6.2.2 Contaminant Preparation

97% N-(tert-Butoxycarbonyl)-L-cysteine methyl ester, abbreviated TCME, was used as the contaminant. The TCME was applied to glass slides in three evenly spaced 5 μ L drops using a micropipette, shown in Figure 29. After application, the slides were placed on supports in the container, shown in Figure 30.

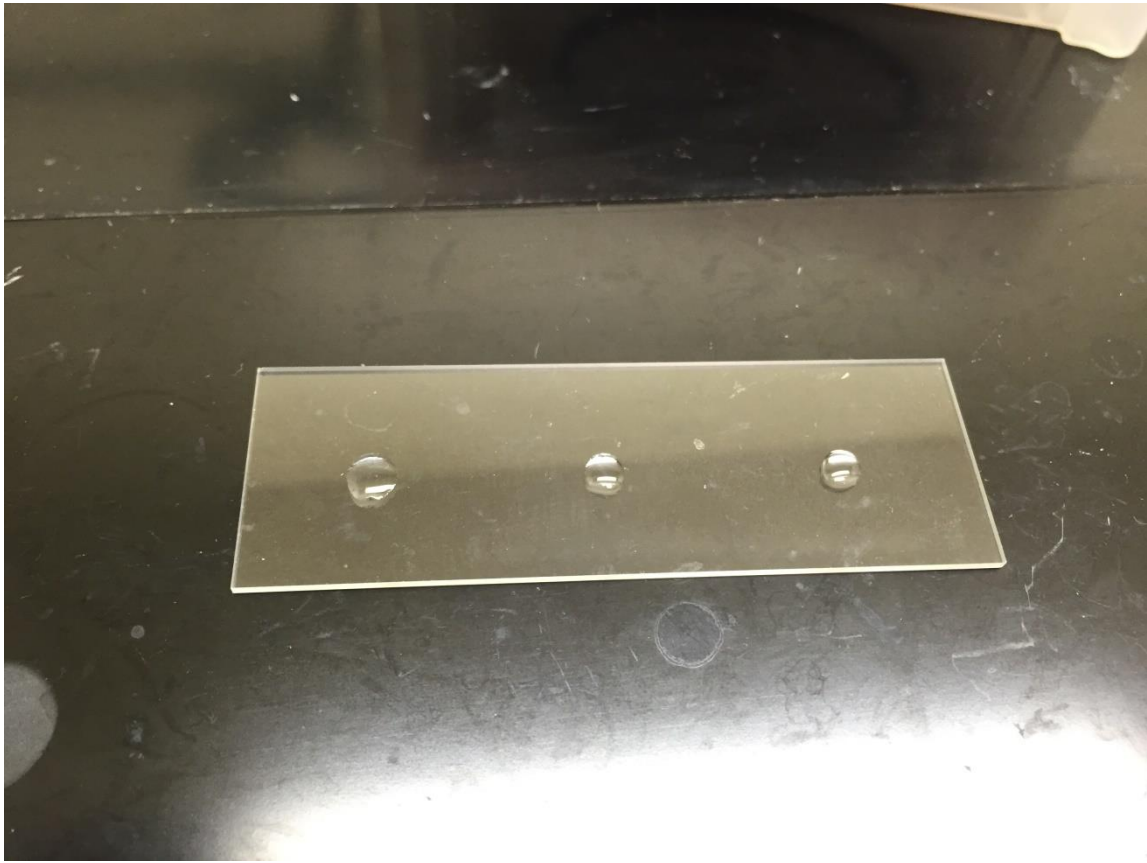


Figure 29. Glass slide with three evenly spaced 5 μ L TCME drops

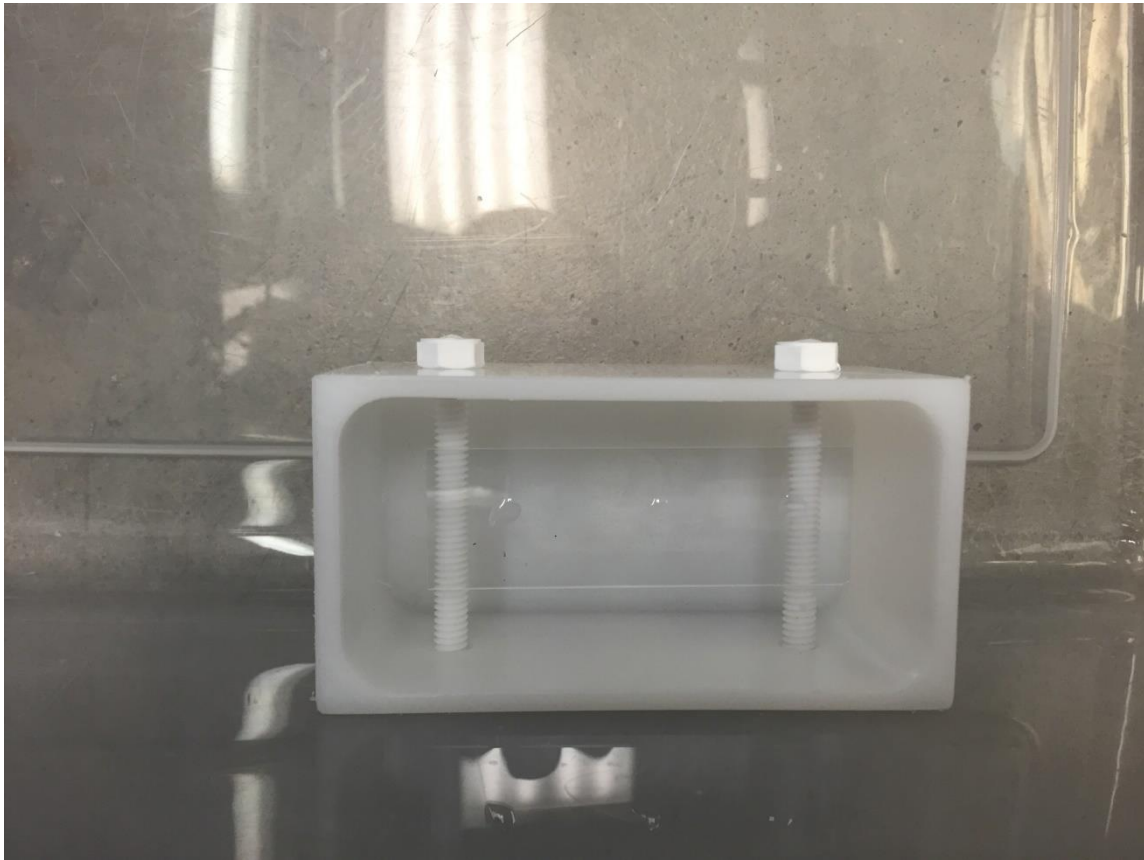


Figure 30. Slide mounted on the slide cradle bolts after TCME application

6.2.3 Decontamination Foam Preparation

The decontamination foam was prepared using industrial high-expansion foam concentrate with added hydrogen peroxide in tap water. The foam concentrate was purchased from Tyco fire protection products and was called C2 High Ex Foam; the concentrate was identical to the foam concentrate used in the liquid phase decontamination trials. The hydrogen peroxide was 30% by volume in water. The decontamination foam was prepared in 2.5 L batches using 100 mL of high-expansion foam concentrate, varying amounts of 30% H₂O₂, and the balance tap water.

6.2.4 *Application of Decontamination Foam*

The trays were mounted to the walls of the HDPE container at heights of 5, 15, and 25 cm from the bottom of the container. The slides were placed on the supports and the container was then filled with foam using the lab-scale foam generator. The foam generator settings were as follows: foam solution pump pressure was 42 psig, the iris damper was set to 2.5% open, and the fan was turned on. Partway through foam generation, the container was rotated to achieve a more uniform fill. Care was taken to rotate slowly to ensure that the slides were not disturbed during rotation.

6.2.5 *Sample Preparation*

The top, middle, and bottom sets of trays were removed 20, 120, and 300 minutes after foam application, respectively. After the trays were removed, they were weighed and compared to their dry weight in order to determine the amount of foam solution that collected in the trays. Additionally, a transfer pipet was used to rinse the excess TCME off the slide to ensure that it was accounted for. Next, 100 μL of foam solution were pipetted into a glass vial containing 1 mL of dichloromethane in order to extract any remaining TCME and stop the oxidation reaction from proceeding. The vials were manually agitated for 30 seconds, then allowed to rest. After 15 minutes, 500 μL of the dichloromethane, TCME mixture was pipetted into GC sample vials for analysis. Because the foam solution which was pipetted into the DCM was present in a separate phase, care was taken to only remove DCM, which is the denser, clear phase, for GC analysis. All samples were run in triplicate for statistical purposes

6.2.6 Analytical Methods

Each sample was analyzed using an Agilent 7890B GC coupled with an Agilent 5977A mass selective detector. The method for these trials used an injection temperature of 250°C, an initial temperature of 45°C held for 3 minutes, a final temperature of 320°C held for 5 minutes, and a ramp of 20°C per minute over 13.75 minutes. The carrier gas was UHP (5.0) helium (Praxair) with a pressure of 23.5 psi and a flow rate of 306 mL/min and the split ratio was 100:1. The column was a HP-5MS (30 m x 0.25 mm i.d., 0.25 µm film thickness). The mass spectrometer was operated in full scan mode (50-550 amu) to identify all possible TCME oxidation products. The GC was calibrated using a series of standard solutions of TCME dissolved in dichloromethane to determine the relationship between peak area and TCME concentration.

6.3 Results and Discussion

6.3.1 Expansion Foam

The target expansion ratio for the decontamination foam was in the range of medium expansion foam (20-200), more specifically between 20 and 75. Initially trials were run without hydrogen peroxide in order to determine the effect of expansion foam on TCME concentration. No reaction was expected to occur due to the lack of an oxidizing agent; however, the foam was expected to dilute the TCME, which is an important factor in determining the remaining TCME. The results from the standard trials are shown in Figure 31.

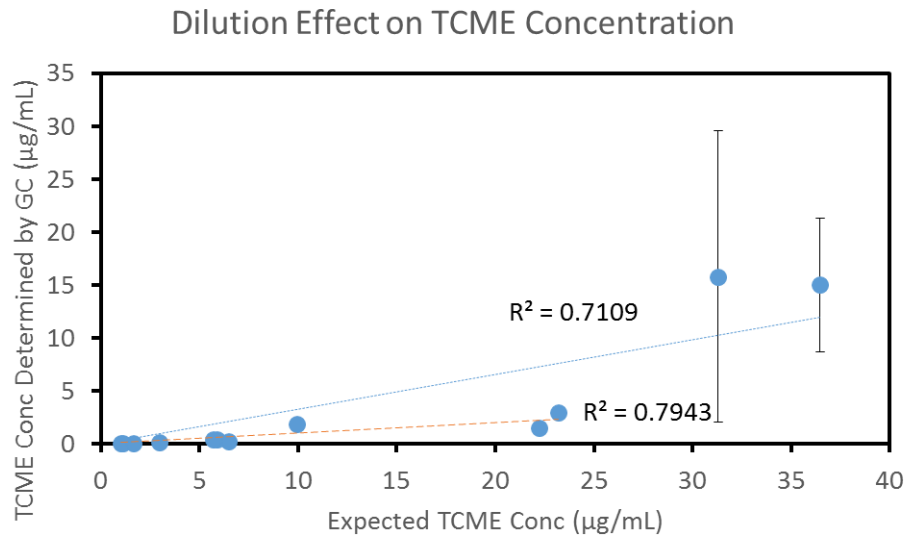


Figure 31. TCME mass calculated based on the dilution due to expansion foam application vs. TCME mass determined by the GC. The upper trend line is a linear fit forced through the origin which was fit for all points. The lower trend line is a linear fit forced through the origin which was fit for all points except the two with the greatest TCME mass.

The formula used in these trials was a modified version of the formula used in the decontamination trials. As described in the materials and methods section, the volume fraction of each component in the decon foam with the highest H₂O₂ content was 66% water, 30% H₂O₂, and 4% HE. Removing the H₂O₂ and replacing it with water would result in an expansion foam solution of 96% water and 4% HE, which forms expansion foam of a very high expansion ratio. Instead the formula was adjusted to use lower amounts of HE, which produces expansion foam that is fairly similar in both stability and expansion ratio to the decontamination foam of the highest H₂O₂ quantity. This formula allows a more direct comparison of the two foams when keeping all foam

generator settings constant. As the main goal was to create a foam with similar dilution properties, this factor was deemed more important than keeping HE content constant.

The relevant foam generator settings, as well as foam characterization, can be seen in Table 10. The expansion ratio of the first standard trial was very low, which was due to the low airflow because the fan was turned off. When the fan was used in the second trial, the expansion ratio increased significantly and fell in the acceptable range, prompting the use of the fan in all future trials. Additionally the stability of the foam was fairly high, collapsing 25 cm in 300 minutes. The foam generator settings from standard trial 2 were maintained throughout the decontamination trials.

Table 10. Relevant foam generator settings, foam solution composition, and resulting foam characteristics. The shaded rows were standard trials which contained no H₂O₂ and the non-shaded rows were decontamination trials

Test No.	Pressure (psig)	Fan Setting	Damper (% open)	Water (vol %)	HE (vol %)	H ₂ O ₂ (vol %)	Mass of foam (kg)	Expansion ratio	Collapse time (min)
1	42	Off	2.5	98	2	0	4.37	13	300
2	42	On	2.5	98.5	1.5	0	1.69	33	300
3	42	On	2.5	66	4	30	1.04	54	300
4	42	On	2.5	91	4	5	1.08	52	270
5	42	On	2.5	95	4	1	1	56	270
6	42	On	2.5	95.9	4	0.1	0.62	90	180
7	42	On	2.5	95.96	4	0.04	0.62	90	180

6.3.2 Decontamination Foam Characterization

The two areas of focus in these trials were the characterization of the decontamination foam and the reactive properties of the foam. From a foam characterization standpoint, the foam performed well. The collapse time in all of the

decontamination trials was at least 180 minutes to collapse 25 cm. A decrease in H_2O_2 content is correlated with a decrease in stability and an increase in expansion ratio. At H_2O_2 percentages 1% and above, the foam has very similar expansion ratio and collapse time; however, with H_2O_2 percentages 0.1% and 0.04% the expansion ratio spikes and stability decreases even keeping the foam generator settings identical. Figures showing the collapse of the foam in the decontamination foam container are shown below.

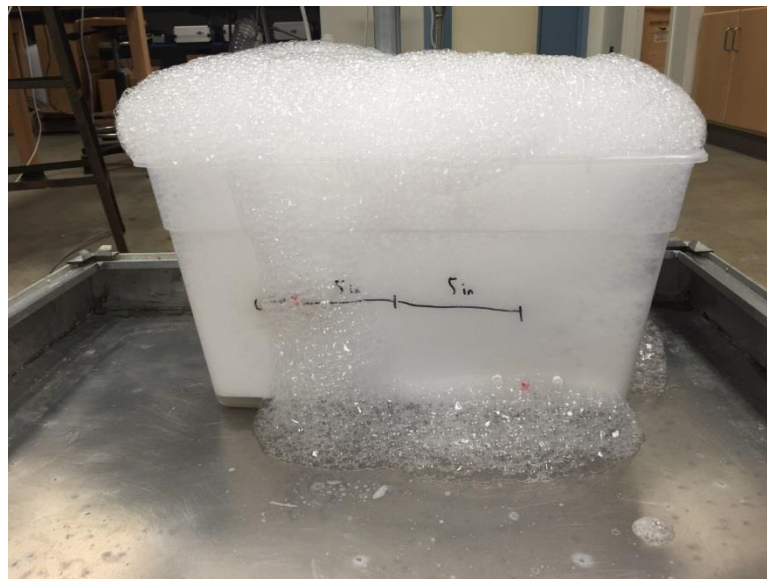


Figure 32. Pictures taken of foam container immediately after decontamination foam application

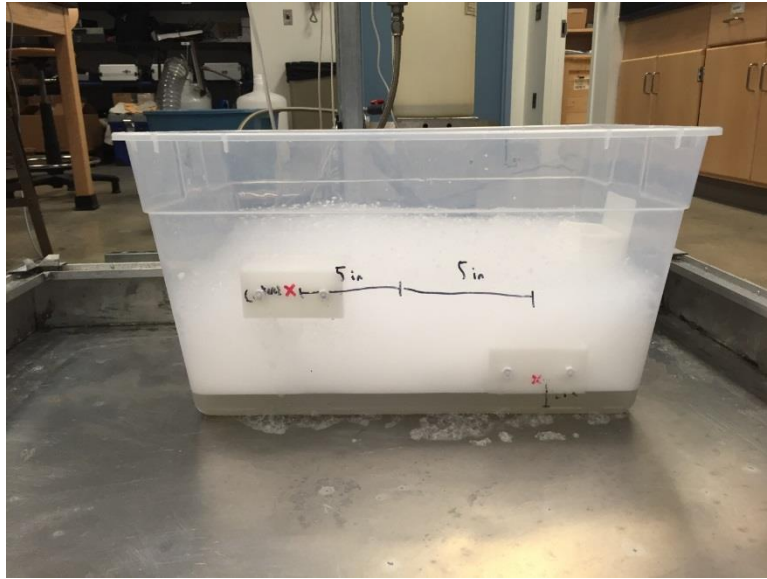


Figure 33. Picture taken 2 hours after decontamination foam application, just before the second set of slides were removed

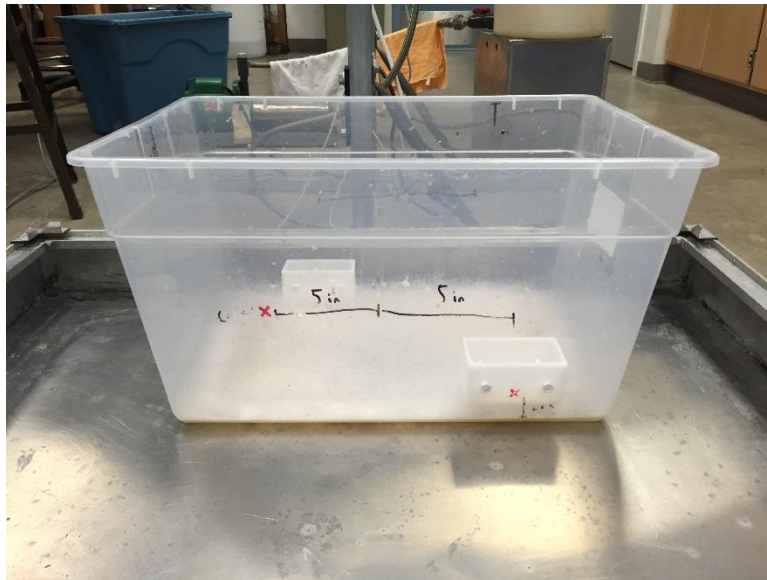


Figure 34. Picture taken 5 hours after decontamination foam application, just before the last set of slides were removed

6.3.3 Decontamination Reaction Quantification

The precipitation of the TCME dimer was again an issue in determination of the decontamination effectiveness. As in the liquid phase decontamination experiments, TCME content in decon trials was compared to TCME content in standard trials to determine the change in TCME concentration, which was used to determine the extent of reaction. Example chromatograms are shown in Figure 35.

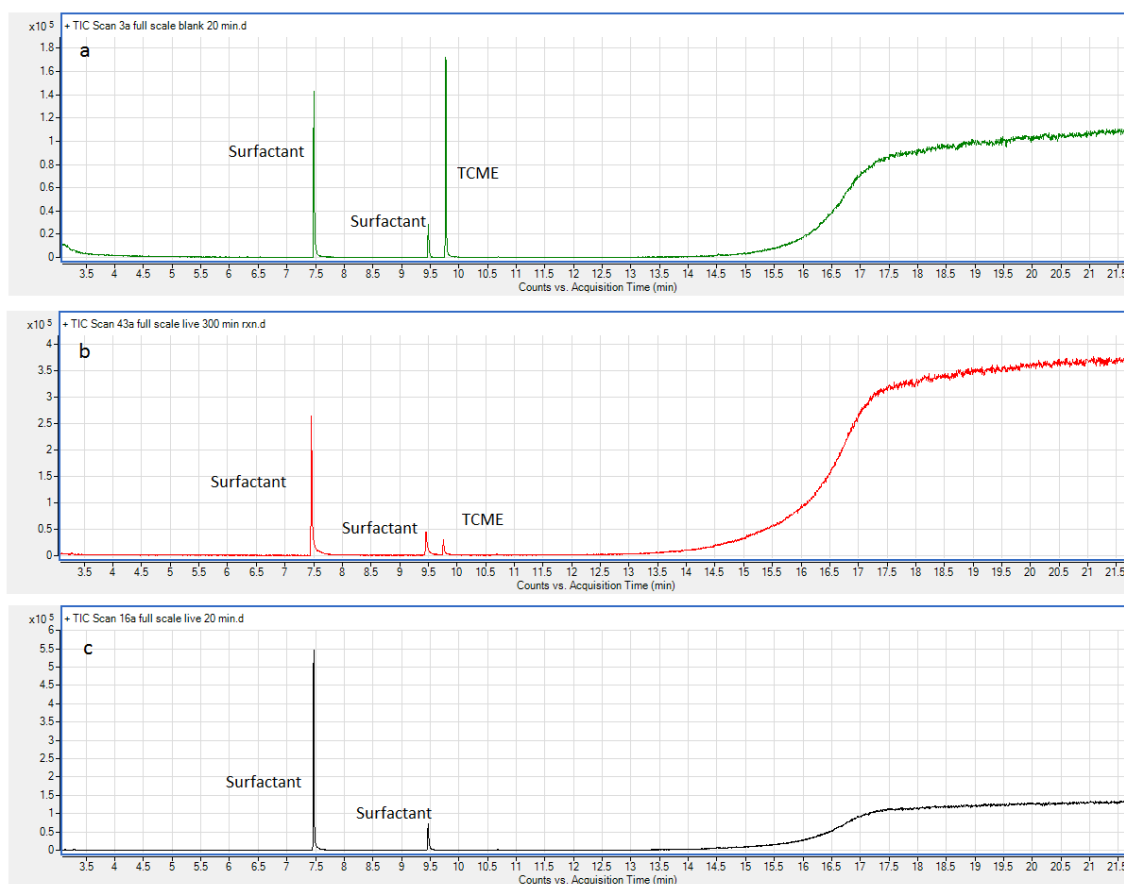


Figure 35. Chromatograms of three different GC trials; (a) TCME, FS solution removed after 20 minutes with no reaction, (b) TCME, DFS solution with 0.04% H₂O₂ removed after a 300 minute reaction period, (c) TCME, DFS solution with 30% H₂O₂ removed after a 20 minute reaction period.

Initially 30 vol% H₂O₂ solution was used in the decontamination foam formula. This quantity is originally based on the formula for Decon Green ⁵² and was used in liquid phase decontamination trials by Harding *et al.* ⁶³. The complete results of decontamination trials are shown in Figure 36. It was expected that at this quantity of H₂O₂ the decontamination reaction would partially occur; however, the reaction proceeded to completion at even the 20 minute reaction time. In previous work on the liquid phase decontamination, H₂O₂ present in 250 times the stoichiometric amount to completely convert TCME into TCME dimer required was unable to achieve better than 99% decontamination after 24 hours. In a similar scenario, using the foam generator, complete decontamination occurred in 20 minutes with only 14 times the required stoichiometric amount. This is likely due to the catalytic behavior of transition metals in cysteine oxidation ⁶⁴.

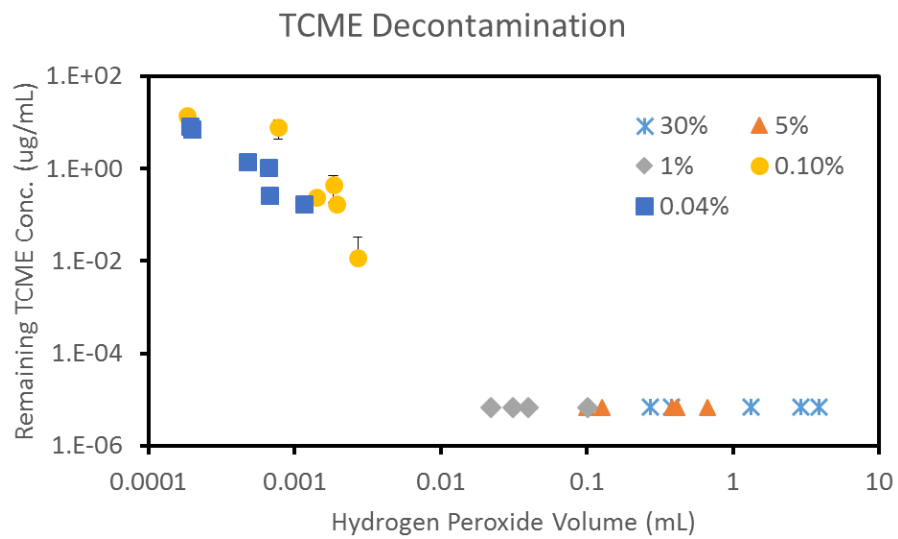


Figure 36. Decontamination trials conducted at 5 different H₂O₂ amounts with error bars showing standard deviation

As shown in Figure 36 all trials with H₂O₂ concentrations above 1% reached complete decontamination; however, trials below 0.1% experienced little to no decontamination, as shown in Figure 37. The dashed black curve represents the fit generated in Figure 31 using the standard solutions. For both concentrations, at the 20 minute time point the TCME concentration is above what would be expected even if there was no reaction (due to dilution). All 120 and 300 minute reactions fall below the expected concentration, suggesting that decontamination was able to occur when the allotted time was longer. Additionally, trials with 0.1% H₂O₂ have lower remaining TCME concentrations than those with 0.04% H₂O₂.

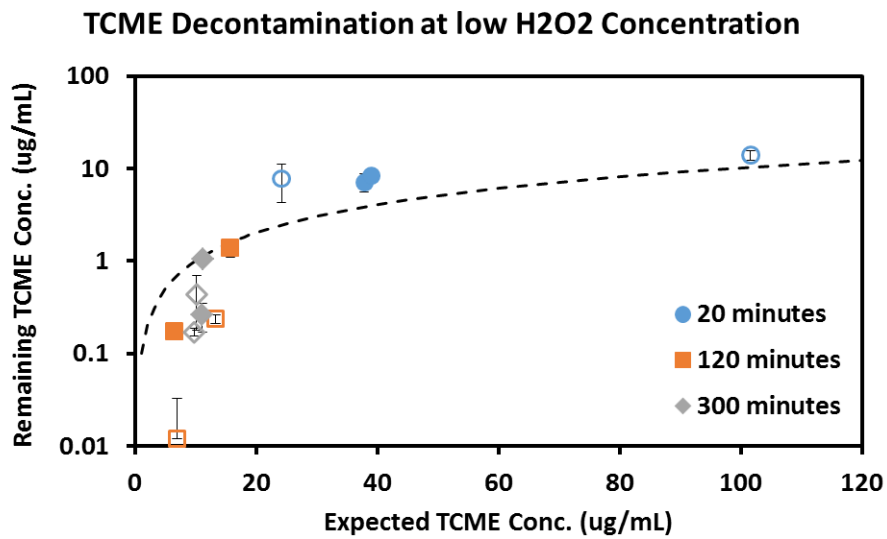


Figure 37. Decontamination trials conducted with 0.1 vol% (solid markers) and 0.04 vol% (hollow markers) H₂O₂. The dashed black curve is the linear fit generated from the standard solutions in Figure 31.

6.4 Conclusions

TCME was able to be thoroughly decontaminated using decontamination foam produced from a lab-scale foam generator. At H₂O₂ concentrations as low as 14 times the stoichiometric amount complete decontamination was achieved in times as low as 20 minutes. Below this point, partial decontamination was achieved, which was a function of both H₂O₂ amount and reaction time. Compared to previous trials conducted in glass vials the decontamination using the foam generator far outperformed expectation; however, this was likely due to the catalytic nature of iron and other metals which could have leached into the DFS from the piping.

Compared with realistic application, typically decon foam is applied in great excess in order to ensure decontamination. Therefore requiring 14 times excess is not a

barrier to the use of this technology. Additionally, foam produced in these trials had high stability and an expansion ratio that fell in the acceptable range, meaning that it could potentially be used in an actual industrial hazardous chemical spill scenario.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This work studied the application of decontamination foam to hazardous chemical spills in industry in three phases; foam generation, liquid phase decontamination, and decontamination using a foam generator. The study on foam generation included developing and constructing a foam generator which could produce high-expansion foam that was similar to foam produced in industry. The study on liquid phase decontamination observed the interaction between decontamination technologies and an analog of industrial contaminants. The study of decontamination using a foam generator applied decontamination foam in a way similar to industrial application to show the feasibility of this technology in real world application.

7.1.1 *Foam Generation*

Due to issues with industrial-scale foam generators, a foam generator was developed in this work. The aim of the foam generator was to produce high-expansion foam with good stability characteristics at low foam production rates. The foam generator constructed in this work was able to produce foam with expansion ratios ranging from approximately 300-900 and a time to half-height of approximately 185 minutes. The foam generator was also designed to be very customizable, which is useful in a laboratory setting. Additionally it was designed to be inherently safer by changing the pressure source and the piping configuration.

7.1.2 Liquid Phase Decontamination

Decontamination has received a great deal of attention in military applications resulting in the publications of a series of works, mainly patents by military research labs. Despite the similarities between military and industrial decontamination, research on the industrial side is severely lacking. Additionally, work done previously either used polar contaminants which dissolved easily in the foam solution or used non-polar contaminants, but ignored the transport limitations imposed by differences in the polarity of the foam solution and the contaminant. This work focused on a contaminant that was a surrogate for hazardous industrial biochemical. The contaminant was a protected derivative of cysteine, which had a low solubility in foam solution, allowing the study of decontamination of non-polar contaminants. In this work incubation time was changed prior to H₂O₂ application. As incubation time increased, decontamination improved both in the rate of reaction and the concentration 24 hours after application. Additionally, the effect of surfactant on liquid phase decontamination was studied. The surfactant had no significant effect on the solubility of the contaminant in the solution; however, it did have an effect on decontamination, improving both the reaction rate and final concentration.

7.1.3 Decontamination Using the Foam Generator

In previous work foam was applied to contaminants using manual application. This approach is easy to execute, but ignores the effects of foam handling on the structure and characteristics of the foam. In order to more realistically study decontamination, a foam generator was used to produce foam. The characteristics of

decontamination foam produced by the generator were acceptable, with expansion ratio between 50 and 90 and collapse times of 300 to 180 minutes for 25 cm. The foam was able to react to completion with the contaminant at much lower than expected amount of H₂O₂. In liquid phase decontamination the H₂O₂ was present at 250 times the stoichiometric amount, and in many cases contaminant remained after 24 hours. Using the foam generator, complete decontamination occurred using 14 times the stoichiometric amount of H₂O₂ in as little as 20 minutes, due to the catalytic properties of metals which leached into the foam from the piping. These results confirmed the proof of concept that decontamination foam application to a realistic spill scenario was feasible.

7.2 Recommendations for Future Work

7.2.1 Foam Production

To this point the foam generator was used primarily to generate foam, and characterization efforts have been mostly neglected. Foams used in these trials were not modified to look at important characteristics from a foam generation standpoint, which is an area that should be expanded in the future. Changes could be made to the amount of foam concentrate or the amount of hydrogen peroxide used in the mixture to assess the contribution to foam stability or other important characteristics such as adhesion to surfaces. Additionally different additives could be tested to increase stability. This variable has been described in literature, and through small adjustments, can be extended greatly^{9,65}. One possible solution to extending the lifetime is the addition of small amounts of xanthan gum (1 g/L). For foams with an initial residence time of 1-10

minutes, the addition of xanthan gum can increase lifetime up to 10 hours⁹. This work was done with foams with very low expansion ratios, and may need to be further adjusted to medium expansion foam applications; however, the concept is one of potential interest. So far these additives have mostly been tested on handmade foams and not foams created using a foam generator, which would increase the understanding of their applicability. Another area of interest is the addition of specific chemicals to aid in the oxidation of contaminants. Work has been done showing that the addition of catalytic amounts of bicarbonate are able to open up additional reaction pathways and enhance the kinetics of cysteine oxidation⁵⁴. To this point, all work has been done in the liquid phase and has not been studied in foams. Although the far-reaching applications of this work may not be applicable to universal decontamination, testing the efficacy of this liquid based research in a foam application may be relevant for other liquid-to-foam transitions. Another area of interest is in more detailed measurements of foam characterization such as foam bubble size, foam bubble wall thickness, and quarter drain time.

7.2.2 *Entrainment of Chemicals in Foam Matrix*

Maintaining contact until completion of the reaction is crucial to effective decontamination. To this point, there has not been any work examining the length of time that hazardous chemicals remain in the foam matrix. Research in this area would improve understanding of interactions within the foam matrix and would also be more broadly applicable to other types of entrainment.

This problem may be very complex due to issues with solubility of the contaminant in the foam and adhesion of the contaminant on various surfaces. As Love *et al.*⁴ illustrated, substrate type is very important for the decontamination reaction. Substrates such as concrete, ceiling tiles, and carpet which are porous prove much harder to decontaminate than smooth surfaces like windows, tiles, and walls.

7.2.3 *Effect of Foam on Non-Polar Contaminants*

Decontamination reactions can only occur when hydrogen peroxide or another decontaminating chemical makes contact with the contaminant. In order for this contact to happen, the contaminant must be soluble in the solvent used in the foam solution. Typically water is used as the solvent, meaning that non-polar contaminants may not be immediately soluble. Preliminary work conducted by Harding *et al.*⁶³ has shown the importance of solubility in the foam phase. This phenomenon should be studied more thoroughly to determine the rate of decontamination due to the combination of both reaction kinetics and solubility issues.

Potential solutions to issues of solubility may include modifying the surfactant to a chemical that has both hydrophilic and hydrophobic regions which could keep non-polar contaminants in solution allowing them to react with hydrogen peroxide. Additionally, the oxidizer and solvent could be modified to chemicals that are less polar, allowing the contaminant to solubilize more easily.

7.2.4 *Modeling of Reactions in Foam Phase*

To this point, reactions that occur in the foam phase have mainly been studied in the liquid phase. Future work into the modeling of reactions in the foam phase should be

conducted to expand the understanding of decontamination foams. This work can be applied both academically in increasing the understanding of decontamination foam reactions and practically in evaluating the necessary amount of decontamination foam and time required for decontamination of a realistic scenario.

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